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Oxidatively Induced Migratory Insertion of Diphenylacetlyene into an Iridacyclobutane Complex and New Ruthenium η^3-Allyl Complexes for Multicomponent Cycloadditions

by

Andrew Robert Lee Skauge

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A Thesis

submitted to the Faculty of Graduate Studies and Research in partial fulfillment of the requirements of the degree of Master of Science

Department of Chemistry

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The undersigned certify that they have read, and recommend to the Faculty of Graduate Studies and Research for acceptance, a thesis entitled **Oxidatively Induced Migratory Insertion of Diphenylacetlyene into an Iridacyclobutane Complex and New Ruthenium η^3-Allyl Complexes for Multicomponent Cycloadditions** submitted by Andrew Robert Lee Skauge in partial fulfillment of the requirements for the degree of Master of Science.

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Abstract

The reactivity patterns of oxidatively induced cyclization of the iridacyclobutane complex [Cp*Ir(C_3H_6)(PhC≡CPh)] have been probed. Modified reaction conditions revealed some fine subtleties in this chemistry that are not well understood, directing either cyclization or acyclic product formation. The nature of the oxidant is of primary importance.

New ruthenium η^3-allyl templates were constructed, namely [(tripod)Ru(η^3-allyl)CO]$^+BF_4^-$ and [(tripod)Ru(η^3-allyl)Cl] which were unobtainable by straightforward methods. Preliminary reactivity of these compounds with alkynes was investigated.

List of Abbreviations

Bu^n	(C_4H_9), n-butyl
Cp	(C_5H_5), cyclopentadienyl
Cp'	(C_5H_4Me), methylcyclopentadienyl
Cp*	(C_5Me_5), pentamethylcyclopentadienyl
COD	1,5-cyclooctadiene
DIBAL-H	Diisobutylaluminum hydride
H_a or H_{anti}	Allyl *anti* proton
H_c	Allyl central proton
H_s or H_{syn}	Allyl *syn* proton
HOMO	Highest Occupied Molecular Orbital
Hz	Hertz
L	ligand
LUMO	Lowest Unoccupied Molecular Orbital
M	metal
Me	methyl
NMR	Nuclear Magnetic Resonance
OTf^-	Trifluoromethansulfonate
tripod	1,1,1-Tris(diphenylphosphinomethyl)ethane
Tpm	tris(pyrazolyl)methane
Tpm*	tris(3,5-dimethylpyrazoly)methane
THF	tetrahydrofuran
TMS	trimethylsilyl
quat.	quaternary

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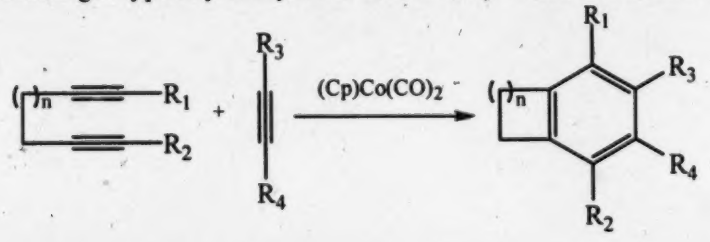
I. General Introduction

A. Background

Organometallic complexes find particular utility in organic synthesis. Some of the most important applications are transition metal-mediated annulation reactions forming carbocycles.[1-4] The synthetic chemist can exploit such reactivity to form more than one carbon-carbon bond in a single pot reaction.[5,6] Reactions at transition metal centers frequently serve as the basis of multicomponent annulations. In many cases, a transition metal can promote nonconcerted cycloadditions by stabilizing several of the reactive organic fragments at one reaction site.[6,7] Other transition metal-mediated annulation reactions involve sequential reactive ligand coordination followed by carbon-carbon bond forming steps. In the latter case, the formation of three or more new carbon-carbon bonds from simple precursors to yield carbocycles can be achieved efficiently via a transition metal template.[6]

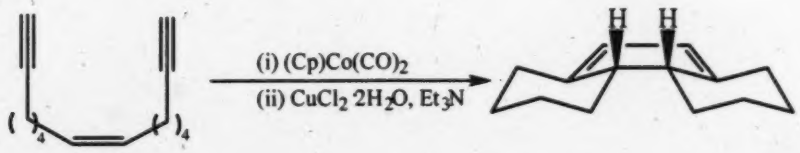
The generation of carbocyclic rings with an even number of carbon atoms has been accomplished by many multiconstituent transition metal-mediated annulation processes. One of the most important of these processes is the cyclooligomerization of alkynes leading to the formation of substituted benzenes and cyclooctatetraenes.[8-10] This process of ring forming is typically catalyzed or mediated by nickel and cobalt. Bicyclic



(Eq. 1)

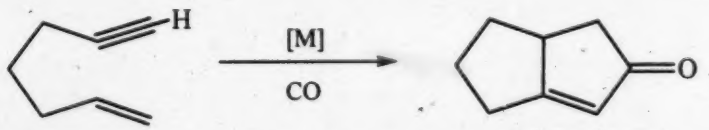
compounds can be formed by using α,ω-diynes (Eq. 1).[11] A similar transformation occurs in the cobalt-mediated cyclotrimerization of two alkynes and one alkene, resulting

in the formation of cyclohexadienes.[12] The intramolecular version of this reaction using enediynes was extensively developed by Funk and Vollhardt (Eq. 2).[13]



(Eq. 2)

In contrast, transition metal-mediated processes offer only a few general methods for the formation of carbocycles with an odd-number of carbon atoms and most of these have focused on the formation of five-membered rings. The Pauson-Khand reaction is one of the most used multicomponent methods for constructing five-membered rings,[12,14-16] typically using complexes of cobalt (eg. $Co_2(CO)_8$).[12] This reaction, a key step in the synthesis of several natural products,[17] generates cyclopentenones by the transition metal-mediated [2 + 2 + 1] cycloaddition of an alkene, an alkyne, and carbon monoxide. Intramolecular versions of this reaction lead to bicyclic products (Eq. 3).[18] The scope of this reaction has been extended to the carbonylative bicyclization of enynes and diynes using zirconium[19] and iron[20] catalysts. More recently, Livinghouse has reported a

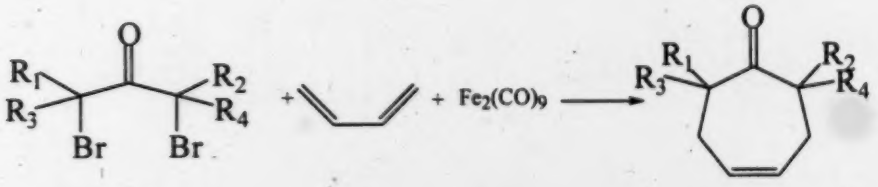


(Eq. 3)

photochemical promotion of the Pauson-Khand reaction using 10 mol% of $Co_2(CO)_8$ at 50-55°C and 1 atm of CO pressure.[21] In 1997, the use of other late metal catalysts was reported by Murai[22] as five-membered rings were constructed with a catalytic amount (2 mol%) of ruthenium ($Ru_3(CO)_{12}$) using dioxane as the solvent and 10 atm of CO pressure at 160°C while Mitsudo,[23] nearly simultaneously, found that under nearly identical conditions, similar reactivity could occur in dimethylformamide (DMF), N,N-dimethylacetamide (DMAc), THF, or toluene.

Other general transition metal-mediated routes to five-membered rings involve [3+2] cycloaddition.[24] An efficient route to cyclopentanes is the transition-metal mediated [3+2] cycloaddition of coordinated trimethylenemethane with electron deficient olefins.[24] More recently, cyclopentanes have been synthesized by nickel-catalyzed, organozinc-promoted carbocyclizations.[25]

Methods to form larger odd-numbered rings by similar routes are not as well developed. From a related route to make cyclopentenones via the iron-promoted reaction of 1,3-dibromo-2-propanone and ethenylbenzene(styrene), Noyori's method was extended to seven-membered carbocycles.[11] The intermediate oxaallyl cation may be trapped with a diene to give cycloheptenones in moderate to good yields (Eq. 4). For this seven-membered carbocycle to form, the diene must adopt a *cis*-configuration and the



(Eq. 4)

dibromoketone must have alkyl, aryl, or halogen substituents at both α and α' ends. This synthetic method is just one of a few methods for constructing cycloheptenones,[11] however, the scope of transition metal-mediated multicomponent synthesis towards seven-membered organic rings is increasing.[7,26]

B. General Research Goals

One goal of our research is to develop new fundamental processes for the formation of odd-numbered carbocyclic rings by using novel combinations of organometallic reactions that link together odd- and even-numbered carbon fragments. The allyl ligand can be viewed as an ideal three-carbon synthon and thus a potentially useful precursor to odd-numbered carbocycles. Allyl-containing complexes are readily

prepared and have been used in a wide variety of synthetic applications.[27-34]

In the first part of this project, better control was sought for the oxidatively induced migratory insertion of diphenylacetylene with the metallacyclobutane [Cp*Ir(C_3H_6)(diphenylacetylene)], to produce a cyclopentene product in good yield. Earlier work by Schwiebert and Stryker established the foundation for this process.[33]

In the second part of this project, the construction of a (L_3)Ru(η^3-allyl)Cl complex, where L_3 is a sterically bulky chelating ligand, was targeted, with the eventual goal of probing alkyne cycloaddition reactions in this system. This compound is new and much exploratory work was necessary to construct this organometallic template.

II: Oxidatively Induced Reactivity of Iridacyclobutane Alkyne Complexes

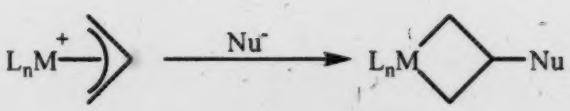
A. Background of Metallacyclobutane Complexes

Since the metallacyclobutane $Cp^*Ir(CH_2CHRCH_2)L$ (L= diphenylacetylene) complexes **1a** (R= H) and **1b** (R= Me) have been made, studies have been conducted towards exploiting the migratory insertion capabilities of these species for the synthesis of organic cyclopentenes.[33]

The low lability of the diphenylacetylene ligand was the reason for selecting this ligand. Metallacycles **1a** and **1b** attribute their stability to diphenylacetylene, whereas the analogous 2-butyne metallacycle complexes are less stable.[35] The repulsive interaction between the electrons in overlapping filled metal and alkyne orbitals should be significantly less for the electron-withdrawing diphenylacetylene ligand compared to the electron-rich 2-butyne. Furthermore, the iridium to alkyne bond should be enhanced by the greater extent of metal to alkyne-π^* back-donation for alkynes with electron-withdrawing substituents.

1) Metallacyclobutane Complexes from η^3-allyl complexes of Transition Metals

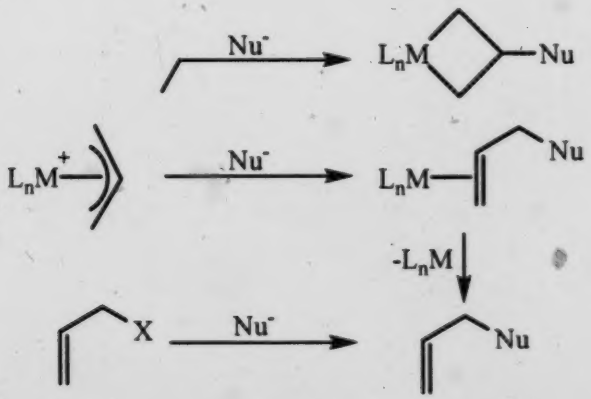
Coordinated allyl complexes have been shown to undergo a wide variety of coupling reactions with one and two carbon units and undergo nucleophilic attack with regioselectivity dependent upon both electronic and steric character of the metal center.[35] Of the many routes to metallacyclobutane complexes,[6,36-45] one of the most straightforward is the conversion of an η^3-allyl ligand to a metallacyclobutane by regioselective nucleophilic attack at the central carbon (Eq. 4).[32,34,46-51] Such reactivity



(Eq. 4)

contrasts that of organic allylic electrophiles and the majority of transition metal η^3-allyl complexes[1,9,27] which undergo addition at either end of the electrophilic three-carbon moiety to effect an overall allylic substitution (Scheme 1).

Scheme 1



Initial attempts to rationalize the unusual kinetically controlled central carbon alkylation involved a charge control argument to suggest that electron-rich π-complexes undergo addition with retention rather than reduction of the valence state of the metal, if possible.[52] That argument relies on a subjective evaluation of the electron-richness of a particular complex. Alternatively, the charge distribution (calculated by perturbational theory) for the allyl ligand indicates that the site of greatest positive charge relative to the terminal carbons may be viewed as the kinetic site of nucleophilic addition which, in this case, is the central carbon of the η^3-allyl (π_3, Figure 1). In typical η^3-allyl complexes, a nodal plane passes through the central carbon of the nonbonding orbital (π_2) which is the highest occupied molecular orbital (HOMO). As such, Davies, Green, and Mingos[1,53]

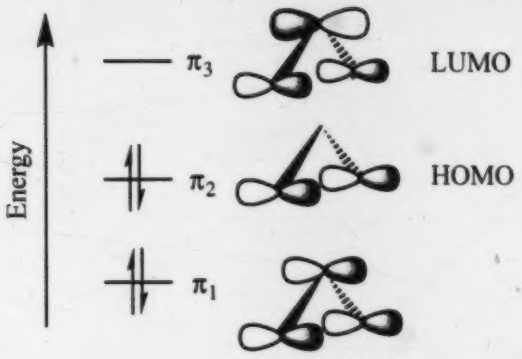


Figure 1: Symmetry and relative energies of the η^3-allyl ligand.

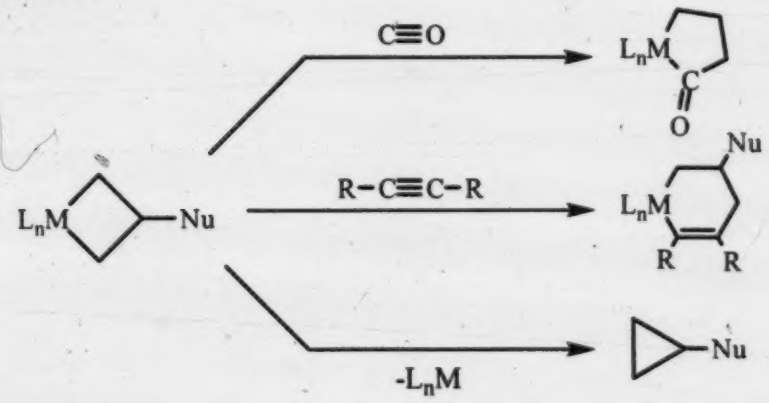
rationalized that $[Cp_2M(\eta^3\text{-}C_3H_5)]^+$ (M=Mo, W) should undergo central carbon addition because an electron-rich metal center will react to retain its high oxidation state (IV) and, at the same time, the central carbon of the allyl is the site of greatest partial positive charge. This charge control perspective was combined with numerous empirical results in a variety of polyenyl-transition metal complexes, leading to the development of general selectivity rules for predicting kinetic nucleophilic addition to cationic π-complexes of transition metals, now known as the DGM rules.[1]

One of the DGM rules states that terminal carbon addition is preferred for odd, open polyenes only if ML_n^+ is a strong electron withdrawing group. Such ambiguity was pointed out by Curtis and Eisenstein, who characterized nucleophilic addition to η^3-allyl complexes in terms of frontier molecular orbital (FMO) control.[54] The metal-based lowest unoccupied molecular orbital (LUMO) is of the correct symmetry to interact with the π_3 allyl molecular orbital in the case of $[Cp_2M(\eta^3\text{-}C_3H_5)]^+$ (M=Mo, W) leading to the prediction of central carbon attack for nucleophilic addition. However, in the case of $[Cp_2M(\eta^3\text{-}C_3H_5)L]^+$ (M=Co, Rh; L = PH_3, CO), simple frontier orbital analysis does not give a definitive prediction for the site of addition to the allyl; Curtis and Eisenstein predict that charge control may govern selectivity in this case.[54] Bergman's discovery of

metallacyclobutane formation by nucleophilic addition to $[CpRh(\eta^3\text{-}C_3H_5)PMe_3]^+BF_4^-$ supports the FMO analysis and again demonstrates the ability of transition metals to modify the electronic character of the η^3-allyl ligand.[44,47]

With carbon nucleophiles, the formation of a new carbon-carbon bond results in transforming the η^3-allyl complex into a metallacyclobutane bearing two metal-carbon σ-bonds, which are potentially amenable to further manipulation (Scheme 2). For example, migratory insertion of carbon monoxide or an alkyne results in the expansion of the metallacycle by one and two carbon atoms, respectively. Coupling of the two α carbons at the metal center would constitute an annulation process, leading to the formation of a cyclopropane molecule.

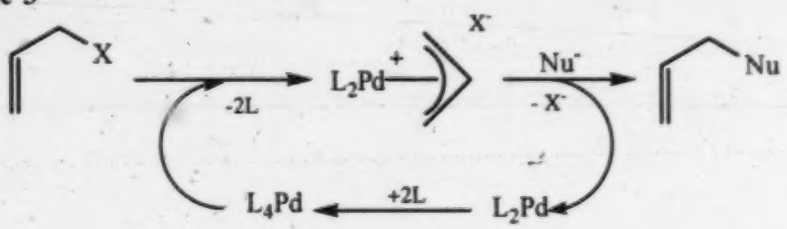
Scheme 2



In 1977, Green produced the first metallacyclobutane complexes derived from η^3-allyl complexes by the reaction of $[Cp_2M(\eta^3\text{-}C_3H_5)]^+PF_6^-$ (M=Mo, W) with sodium borohydride, methyllithium, and allylmagnesium chloride.[52] Since then, there have been many examples of central carbon addition by nucleophiles to η^3-allyl complexes.[32,33,47,55-58]

Nucleophilic addition to the central carbon of η^3-allyl complexes is a rare reversal of the typical electrophilicity of η^3-allyl complexes.[1,3,11] Generally, nucleophilic addition goes to the terminal carbon of the allyl in such transition metal complexes, resulting in the formal reduction of the oxidation state of the metal by two. Allylic alkylations have been well studied particularly in the palladium system, $[Pd(\eta^3\text{-allyl})L_2]^+X^-$ (L = phosphine, phosphite, phosphorus triamide; X = halide, pseudohalide),[11,30,59-61] where the lability of the olefin ligand subsequent to alkylation enables the system to operate catalytically (Scheme 3).[62] This predominant mode of reactivity is largely responsible for the popularity of η^3-allyl complexes in organic synthesis. Nevertheless, by controlling reaction conditions and careful selection of

Scheme 3



X = OAc, O_2CR, O_2COR, OPh, OH, NR_2, SO_2Ph, NO_2

nucleophile, it is possible to obtain products which arise from central carbon addition even to this palladium system.[57,63]

2) Application of Metallacyclobutane Formation to Organic Synthesis

The $[Cp^*M(\eta^3\text{-}C_3H_5)L]^+X^-$ (M= Co) system provides potential for modification and for the ultimate adaptation into organic synthesis. This complex possesses a single coordination site which could be occupied by a variety of ligands at L such as alkynes which could undergo insertion reactions. The $[Cp^*M(\eta^3\text{-}C_3H_5)L]^+X^-$ (M=Rh, Ir) complex is more suitable for investigation than the $[Pd(\eta^3\text{-allyl})L_2]^+X^-$ system because eventual adaptation of metallacyclobutane formation into organic

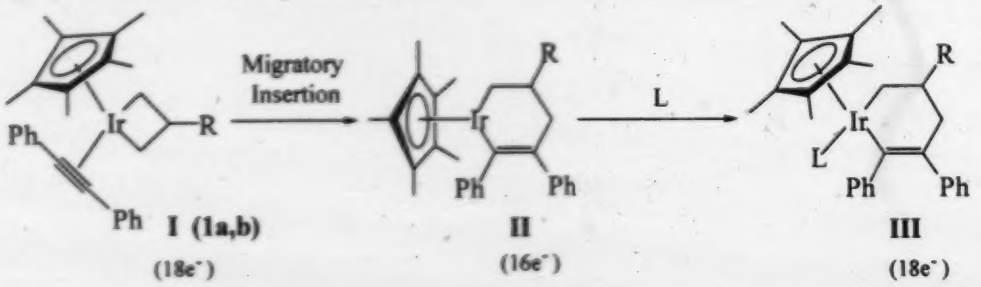
synthesis will require a less expensive metal such as cobalt or iron. For instance, substituting cobalt for iridium in $[Cp^*M(\eta^3\text{-}C_3H_5)L]^+X^-$ in the presence of excess alkyne has been successfully used for the synthesis of metallacycles as intermediates in the formation of coordinated seven-membered rings.[64]

3) Oxidatively Induced Cyclopentene Formation

a) Diphenylacetylene Metallacycle Reactivity

The diphenylacetylene iridacyclobutane complexes **1a** and **1b** are completely unreactive at ambient temperature in benzene or THF, in the presence or absence of added ligand (Me_3P, Ph_3P, CO).[33] These complexes decompose intractably at elevated temperatures or under photolysis conditions.[35] For instance, when the parent metallacycle **1a** is treated with excess triphenylphosphine in benzene at 110°C for three hours, complete decomposition occurs. Even brief photolysis (10 min., 450W) of a solution of complex **1a** in benzene-d_6 results in total disappearance of the starting material without the formation of any spectroscopically identifiable products.

Despite the fact that the diphenylacetylene metallacycles were found to be kinetically inert, migratory insertion reactions were estimated to be thermodynamically favorable for cases where the 16-electron product (**II**) is trapped by a strong donor ligand, L to form the 18-electron product (**III**).[35]



The change of an iridium-sp^3 carbon bond to an iridium-sp^2 carbon bond (**I**→**II**) should be favored by about 20 kcal/mol,[65] while the formation of the new C-C bond (worth about 83-85 kcal/mol),[66] at the expense of changing a $\pi_{C\equiv C}$ bond to a $\pi_{C=C}$ bond, should account

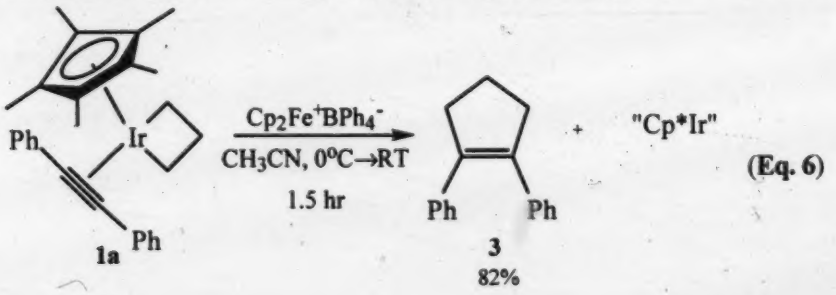
for an additional 54 kcal/mol of stability.[67] In addition, the relief of ring strain from a 4-membered ring to a 6-membered ring should be favorable. Since the migratory insertion into diphenylacetylene metallacycles is expected to be exothermic but with a high activation barrier, Schwiebert and Stryker set out to find conditions to facilitate the insertion at lower than decomposition temperatures. [35]

b) Oxidatively Induced Migratory Insertion

Pronounced rate enhancements upon one electron oxidations have been reported for processes such as ligand substitution and dissociation, reductive elimination, structural isomerization, and migratory insertion.[68-73] Most of the work involving oxidatively induced migratory insertion reactions pertains to CO insertion reactions which form metal acyl complexes, a common reactivity pattern for many transition metal complexes.[1,74] From mechanistic studies by Giering of electrocatalyzed carbonyl insertion into $CpFe(alkyl)(L)_2$ (where alkyl = CH_3, L = CO, PPh_3), oxidation provides a 10^{11} fold increase in the rate of insertion.[75,76] Without an oxidant, the insertion reaction (equation 6) is found not to proceed.[33,77] Absolutely no examples were known of oxidatively induced migratory insertion reactions of unsaturated hydrocarbons into metal-alkyl bonds until Schwiebert and Stryker reported such processes in 1994.[33]

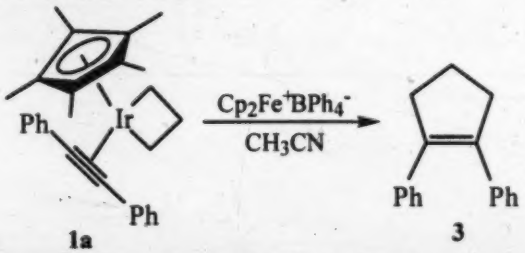
c) Features of the One-Electron Oxidation

Schwiebert and Stryker found that migratory insertion reactions in iridacyclobutane complexes **1a** and **1b** can be *induced* by treatment with one-electron oxidants.[33] They discovered that adding an excess of $Cp_2Fe^+BPh_4^-$ (**2a**$^+$) to the parent-



(Eq. 6)

metallacycle **1a** in acetonitrile (0°C→RT, 1.5 hr) resulted in the formation of 1,2-diphenylcyclopentene (**3**) and an ambiguous pentamethylcyclopentadienyl iridium complex (Eq. 6).[35] The cyclopentene could be isolated in 70-85% yield after purification by flash chromatography on silica gel and was spectroscopically identical to a standard sample prepared using 1,5-diphenyl-1,5-pentanedione and a low valent titanium complex.[78] The highest yields of cyclopentene were obtained if the reaction temperature was somewhat lowered and excess oxidant (>2 equiv.) were used (see Table 1). Excess oxidant was required probably because of the instability of the ferricinium tetraphenylborate at room temperature, because $\mathbf{2a}^+$ is known to deteriorate immediately on dissolution in acetonitrile.[79] The low temperatures minimized the extent of side reactions and maximized the yield of cyclopentene **3** (Table 1). Schwiebert had noted that traces of propene and diphenylacetylene are occasionally present when the oxidation reaction is carried out in a sealed vessel.[35]



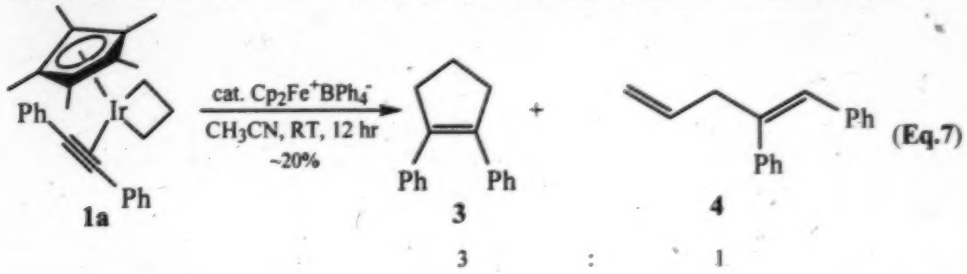
1a **3**

Table 1: Influence of Reaction Conditions on the formation of **3**[35]

Temperature (°C)	Reaction Time(hr)	Yield (%)
-35	10.5	44
0	10.5	68
0→RT	1.5	82
RT	15	69

Although the insertion reaction is induced by the oxidant, it cannot be made catalytic in oxidant. When sub-stoichiometric amounts of $Cp_2Fe^+BPh_4^-$ (0.3 eq.) are used to oxidize **1a**, the acyclic diene **4** is produced as a significant by-product (**3/4** ~ 3:1) with a

low overall yield (<20%, Eq. 7).[35] Schwiebert noted that the starting material was completely consumed but no other organic products (eg. cyclopropane, propene) were

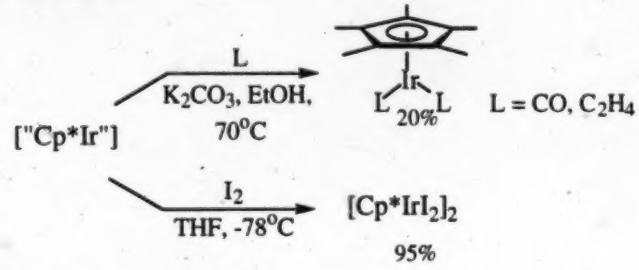


detected in the volatile components of the product mixture as determined by ^1H NMR spectroscopy. Furthermore, no organometallic complexes containing ligands other than C_5Me_5 were detected by ^1H NMR spectroscopy. Even though the cyclopentene **3** and diene **4** are inseparable by flash chromatography, the diene **4** is easily identified by comparison of the proton NMR to that of an authentic sample, which can be prepared from the reaction of diphenylacetylene with DIBAL-H followed by treatment with allyl bromide.[80]

The composition of the iridium complex subsequent to release of the organic moiety is not clear.[35] Several unidentified, diamagnetic Cp*Ir fragments were observed in the product mixture. In attempts to recover the iridium, the parent metallacycle **1a** was oxidized in the presence of excess ligand (L= PPh_3, CO, or C_2H_4), leading to the formation of minor amounts (<20%) of the known complexes Cp^*IrL_2 (L= PPh_3 (**5**),[55] L= CO (**6**),[81] L = C_2H_4(**7**)[82]), with little effect on the yield of cyclopentene **3** (Eq. 7). Similar results were obtained upon reduction of the crude reaction mixture with basic ethanol under an atmosphere of CO or ethylene, standard conditions for the conversion of the Ir(III) complex $[(Cp^*)IrCl_2]_2$ (**8**) to the corresponding Ir(I) bis(ligand) complexes.[82] Conversely, an oxidative workup of the crude organometallic products with excess iodine at -78°C in THF returns the metal in near quantitative yields as $[Cp^*IrI_2]_2$ (**9**)[83] (Scheme 4). This oxidative workup also has little effect on the yield of cyclopentene **3**. Since a strong oxidant is required to generate a useful organometallic complex of iridium, this

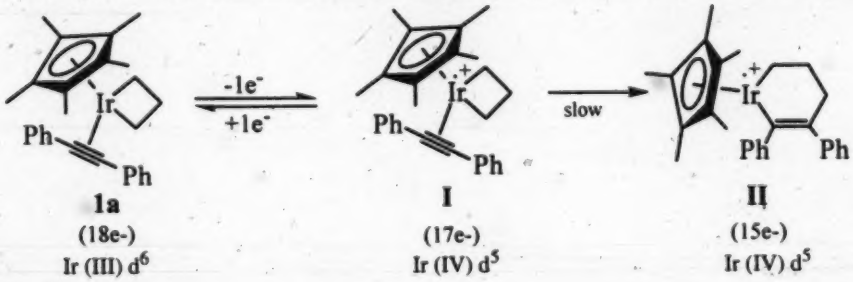
suggests the presence of a metal-metal bonded species (ie. "Cp*Ir" aggregates) resulting from the insertion/reductive elimination reaction in the oxidized complex.

Scheme 4



d)Electrochemical Studies

To assist in constructing a plausible mechanism, Schwiebert conducted electrochemical studies.[35] Cyclic voltammetry of the parent metallacycle **1a** in 0.2M $Bu_4N^+BF_4^-$ in acetonitrile shows an oxidation wave at 0.03V versus the ferrocene/ ferricinium couple at scan rates from 500 to 2000 mV/sec. Although, the peak anodic to peak cathodic separation for this oxidation wave is larger than the theoretical value for a reversible wave ($\Delta E_{observed}$ = 0.08 V, $\Delta E_{calc.}$ = 0.06V), the oxidation is presumed to be reversible at scan rates greater than 500 mV/sec since the separation of the peaks remains constant at a variety of scan rates (also the anodic and cathodic currents will be of equal magnitude in a reversible process).[35,84] A control experiment showed that the peak anodic to peak cathodic separation for the ferrocene/ferricinium couple (known to be reversible at 500 mV/sec) was also 0.08V when measured under the same conditions. With no waves corresponding to the reduction of other downstream radical intermediates observed, it was concluded that the initial oxidation is rapid relative to subsequent



1a (18e-) Ir (III) d^6 — **I** (17e-) Ir (IV) d^5 — **II** (15e-) Ir (IV) d^5 **(Eq. 8)**

migratory insertion (Eq. 8) and is likely reversible since the difference between the ferrocene and parent metallacycle is very small. A second irreversible oxidation wave is observed at 0.47V relative to the ferrocene/ferricinium couple, suggesting that complex **1a** is subject to over oxidation by strong oxidants. This was corroborated by treatment of metallacycle **1a** with stronger oxidants such as silver triflate or acetylferricium, which results in complete consumption of the starting material without formation of identifiable organic products.

The reactivity of the radical cation **I** (Eq. 8) is much greater than the neutral complex **1a**. Because the 18-electron metallacycle alkyne complexes do not undergo migratory insertion, it is impossible to calculate the rate enhancement provided by the oxidation to the corresponding 17-electron complex. Generally, the lability of the 17-electron complex (**I**) towards insertion is attributed to the potential for coordination of an additional ligand to form a 19-electron species which undergoes facile migratory insertion in order to lower the electron count at the metal.[72] Typically, the rates of interconversion from 17 to 19 electron organometallic radical complexes are much higher than those for 16 to 18-electron interconversions of their closed shell counterparts. This has been suggested to arise from a three-electron attractive interaction between an incoming ligand and the singly occupied orbital in a 17-electron complex, which leads to a doubly occupied bonding orbital and a singly occupied anti-bonding orbital.[85-88] This half bond order stabilizes the 19-electron complex, providing a driving force for the interconversion. Besides considering that solvent could behave as a ligand for the metallacycle diphenylacetylene radical intermediate **I** (Eq. 8), there exists the possibility that the alkyne could donate a second pair of electrons to make a 19-electron complex. Providing that the conversion of the alkyne from a two to a four-electron donor is facile and geometrically reasonable, the rapid intramolecular transformation from 17 to 19-electron complex should dramatically increase the rate of migratory insertion.

e) Solvent Effects

After the initial insertion of the parent metallacycle diphenylacetylene complex **1**, the solvent becomes intimately involved, presumably serving to stabilize electronically or coordinatively saturate an intermediate. When solvents other than acetonitrile (eg. CH_2Cl_2, THF) were used, significantly lower yields of organic products and competitive formation of diene **4** (the product of β-hydrogen elimination after the alkyne insertion) were reported.[35]

f) Effect of Added Ligand

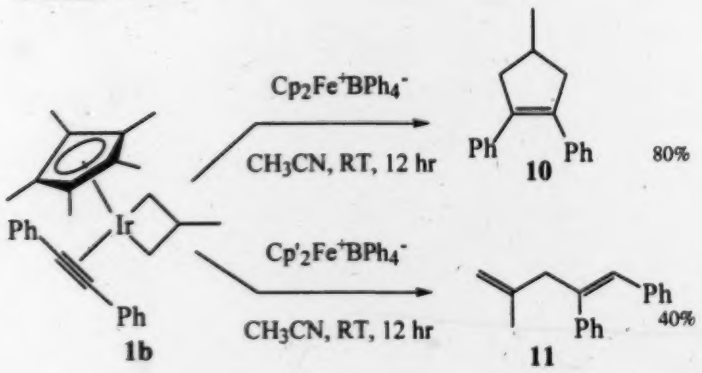
When excess carbon monoxide is used in acetonitrile, only a minimal influence on the product mixture was observed by ^1H NMR spectroscopy. This suggests that the added ligand does not effectively compete with the solvent for coordination to the metal.[35] When more electron-donating ligands (trimethylphosphine and diphenylmethylphosphine) are used, their effects were more difficult to gauge. The trimethylphosphine and diphenylmethylphosphine react rapidly and exclusively with the oxidant, $Cp_2Fe^+BPh_4^-$, thereby preventing oxidation of the parent iridacyclobutane complex. However, oxidation of the parent metallacycle does occur with triphenylphosphine since the latter reacts much more slowly with the oxidant. Even in the presence of excess triphenylphosphine in acetonitrile, cyclopentene formation remains exclusive and high yielding.[35] When the oxidation of the parent metallacycle **1a** is performed in neat pyridine, no identifiable products are detected by ^1H NMR spectroscopy. Pyridine is potentially a strong enough ligand to trap some paramagnetic organometallic intermediates formed after the alkyne insertion, although the identification of these products was not pursued.[35]

When these last two points are consolidated, it is clear that a coordinating solvent or added ligand is necessary to stabilize the unsaturated radical intermediates in order to obtain the organic products. In the absence of adequate stabilization, poorly understood side reactions strongly compete with the desired pathways.

g) Oxidant Dependence

Since the distribution of products from the electrocatalyzed insertion reaction is dependent strongly on the potential of the oxidant, it is critical to control this potential. Schwiebert reports that $(C_5H_4Me)_2Fe^+BPh_4^-$ is approximately 0.1V weaker an oxidant than ferricinium complex **2a**$^+$ and its use favors the formation of the acyclic diene **4** over the cyclic product **3** by a ratio of 2 to 1 at room temperature in acetonitrile (but in a low overall yield ~ 20%).[33] With the reaction performed at room temperature, the starting material is completely consumed and no recognizable organometallic complexes containing ligands other than Cp* are discernible in the ^{1}H NMR spectrum. Reactions with the β-methyl iridacyclobutane **1b** clarify this dichotomy: using the stronger oxidant, ferricinium cation **2a**$^+$, exclusive formation of 1,2-diphenyl-4-methylcyclopentene (**10**) is observed in high yield, while the use of $(C_5H_4Me)_2Fe^+BPh_4^-$, the weaker oxidant, results only in the formation of diene **11**, in much lower yield (Scheme 5).[35] This dramatic effect on reactivity by slight changes in the potential of the oxidant on the product distribution is unique.[33] Attempts to reproduce this reactivity manifold confirming the outer-sphere

Scheme 5

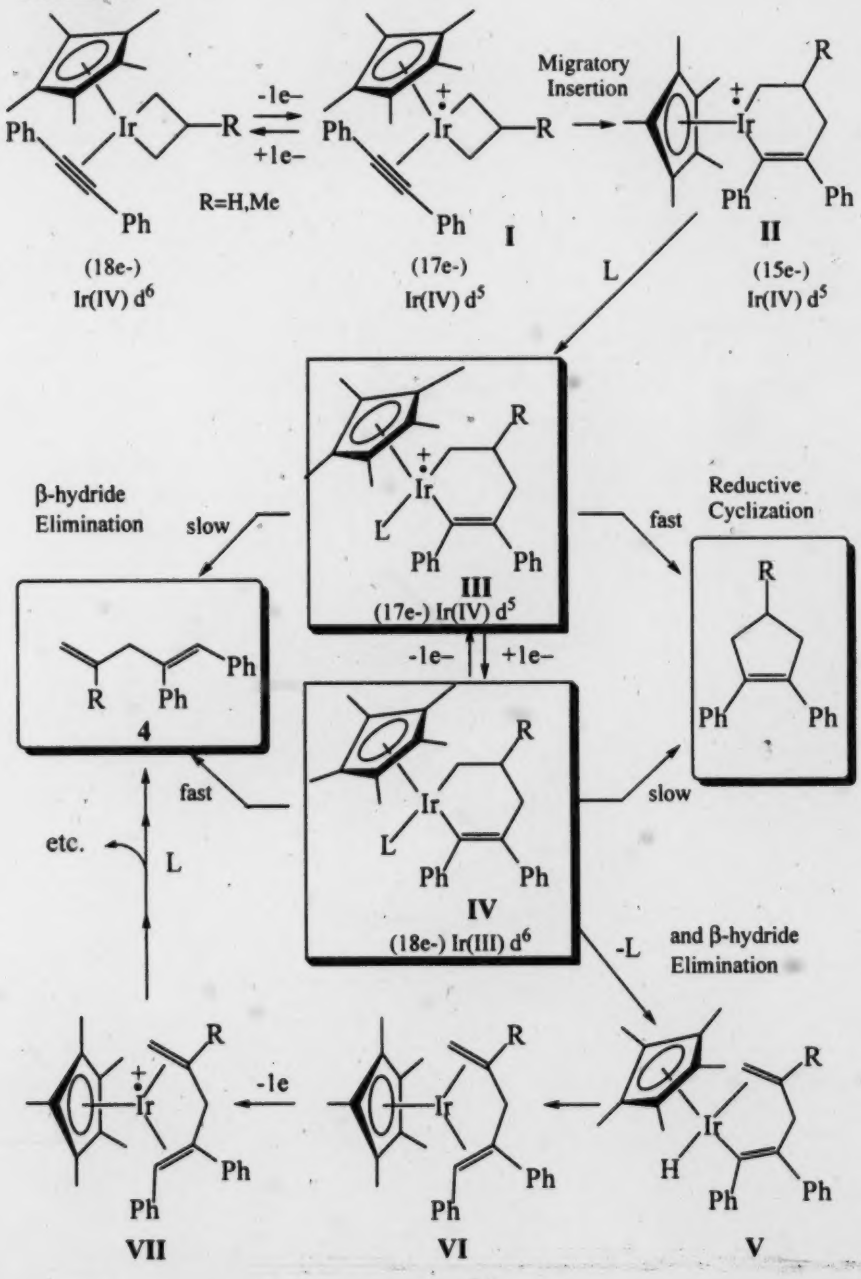


character of the oxidation, by bulk electrolysis at controlled potential failed, resulting in no isolable organic fraction.[33]

h) Plausible Mechanism

Schwiebert and Stryker proposed a mechanistic rationale consistent with the observed effects of solvent, added ligand, and potential of the oxidant (Scheme 6).[33]

Scheme 6



They propound that the product distribution is determined after the alkyne insertion by the rate and extent of back reduction to the even electron manifold (**III**→**IV**, Scheme 6). The formation of cyclopentene or diene arises from inherent differences in the activation barriers to reductive elimination and β-hydrogen elimination from within the odd and even electron manifolds. Reductive cyclization (elimination) from the electron deficient iridacyclohexene **III** in the odd-electron manifold is suggested to be more facile (to form **3**) than β-hydrogen transfer which ulitmately forms **4**. In the relatively electron rich even-electron manifold, however, **IV** preferentially undergoes β-hydrogen elimination leading to **4**, which is consistent with the more conventional reactivity pattern observed for metallacyclic complexes.[89,90] The critical back-reduction (**III**→**IV**) in the electrocatalyzed alkyne insertion reaction is mediated by the conjugate of the original oxidant. In the case of the weaker reductant, ferrocene, the reaction is maintained in the odd-electron manifold (**III**), selectively producing cyclopentene, whereas 1,1'-dimethylferrocene more efficiently mediates back-reduction to the even electron manifold (**IV**), where partitioning favors diene formation.[33]

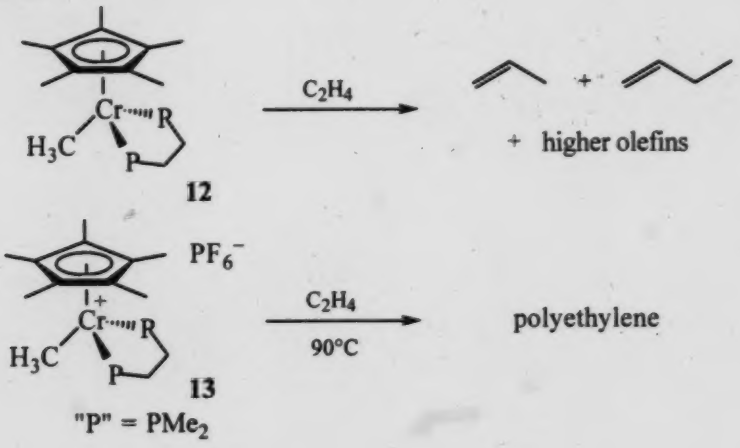
The mechanistic rationale proposed in Scheme 6 is consistent with the observed solvent and ligand effects. Acetonitrile coordination stabilizes the radical cation **III** (L = CH_3CN) toward reduction, helping to maintain the reaction in the oxidized manifold. If the donor solvent is replaced with the π-acidic carbon monoxide in a noncoordinating solvent, the reduction potential of **III** is expected to increase and destabilize this intermediate; return to the even-electron manifold occurs where selective diene formation is observed.[33]

The proposal in Scheme 6 supports the need for rapid, stoichiometric oxidation to obtain cyclopentene selectively. To elaborate, using a catalytic amount of oxidant, slow addition techniques, or bulk electrolysis, the remaining neutral iridacyclobutane complex can function as the reductant for highly electron-deficient complex **II** and/or ring expanded complex **III**, leading to destructive over oxidation of starting material and return to the

even-electron manifold (and diene formation), respectively. The low yields obtained from reactions leading to the diene can be ascribed to both a slower oxidation with the weaker oxidant and to an unfavorable partitioning in the presumed oxidative process that releases the diene from the substitutionally inert[81] Ir(I) intermediate.[33] In more detail, once **IV** loses the stabilizing ligand L (eg. acetonitrile or CO), β-hydride elimination can readily occur thereby forming **V**. Reductive elimination of the metal-hydride complex **V** would then afford the Ir(I) diene complex **VI**. Complex **VI** further oxidizes to the radical cation **VII** (or dication) and subsequent displacement of the diene (**4**) is assisted by ligand association; the fate of the metal is not known.[35]

Related pairs of odd and even electron complexes have shown similar differences in reactivity. As a case in point, the sixteen electron Cr(II) alkyl complex **12** undergoes β-

Scheme 7



hydrogen elimination much faster than alkene insertion, whereas the fifteen electron counterpart **13** undergoes rapid multiple alkene insertions to effectuate ethylene polymerization (Scheme 7).[91]

i) Other Oxidation Methods

Further control of both product distribution and yield were the motives for examining other methods of oxidation. Since iodine has promoted reductive elimination of

cyclopropanated organic compounds from several iridacyclobutane complexes in the series $Cp^*\overline{Ir(CH_2CHRCH_2)}L$ (R=alkyl, ketone; L=PR_3, CO, C_2H_4, C_2Me_2),[34,48,49] Schwiebert treated the parent metallacycle with iodine in THF-d_8 or toluene-d_8 at -78°C to form cyclopentene **3** and diene **4** in a 2:1 ratio (yield ~ 25%).[35] (Note: there was no evidence for the formation of propene nor cyclopropane in the ^1H NMR spectrum.) This marked the only instance where iodinolyis of a metallacyclobutane complex resulted in the coupling of the metallacycle moiety with an "ancillary" ligand rather than simple reductive elimination.[34]

The mechanism of iodinolysis is poorly understood but, it could involve the oxidation of the metal center by an inner sphere mechanism involving electrophilic addition of "I^+" to the metal.

The desired organic products were not obtained when other chemical oxidants were used.[92] Silver tetrafluoroborate and acetylferricinium apparently over-oxidized complex **1a** in acetonitrile, giving only a dark oily indiscernible product mixture.[35] Treatment of **1a** with copper(I) chloride gave no reaction, which might have been the result of the low solubility of the salt in acetonitrile. Exposure of the reaction mixture containing the parent metallacycle to air gave a multitude of Cp* containing products without the formation of cyclopentene **3** or diene **4**.

Schwiebert also investigated this reaction using bulk electrochemical oxidation to exclude inner-sphere oxidation and even-electron reaction pathways.[35] The strategy behind this was to control the oxidation to form **III** (Scheme 6) exclusively. Under such conditions, **III** was to be formed without concomitant formation of a conjugate reductant, thereby inhibiting back-reduction of the radical intermediate **III** to the even-electron manifold **IV**; this minimizes the extent of β-hydrogen eliminations and consequently the formation of the acyclic diene. However, these bulk electrochemical experiments failed to yield any of the expected nonvolatile organic products. Electrochemical oxidation is limited by diffusion at the electrode so the oxidation would only proceed a little at a time

therefore, yielding results that would be equivalent to those obtained from slow addition of the oxidant; hence, the need for rapid, stoichiometric oxidation (as mentioned previously). Volatile products, if formed, could not be detected due to the nature of the experiment; the fate of the organic moieties remains undetermined.

B. Project Goals

With the foundation for oxidatively induced coupling of $Cp^*Ir(C_3H_6)$(alkyne) metallacycle complexes now established by Schwiebert, we sought to influence the equilibrium between the odd and even electron manifolds (**III→IV**) in Scheme 6 by adding reductants in with the oxidant(s) under similar conditions. We have succeeded at confirming some of the results of Schwiebert, while also finding other interesting aspects of this delicate partition between the odd and even electron manifolds.

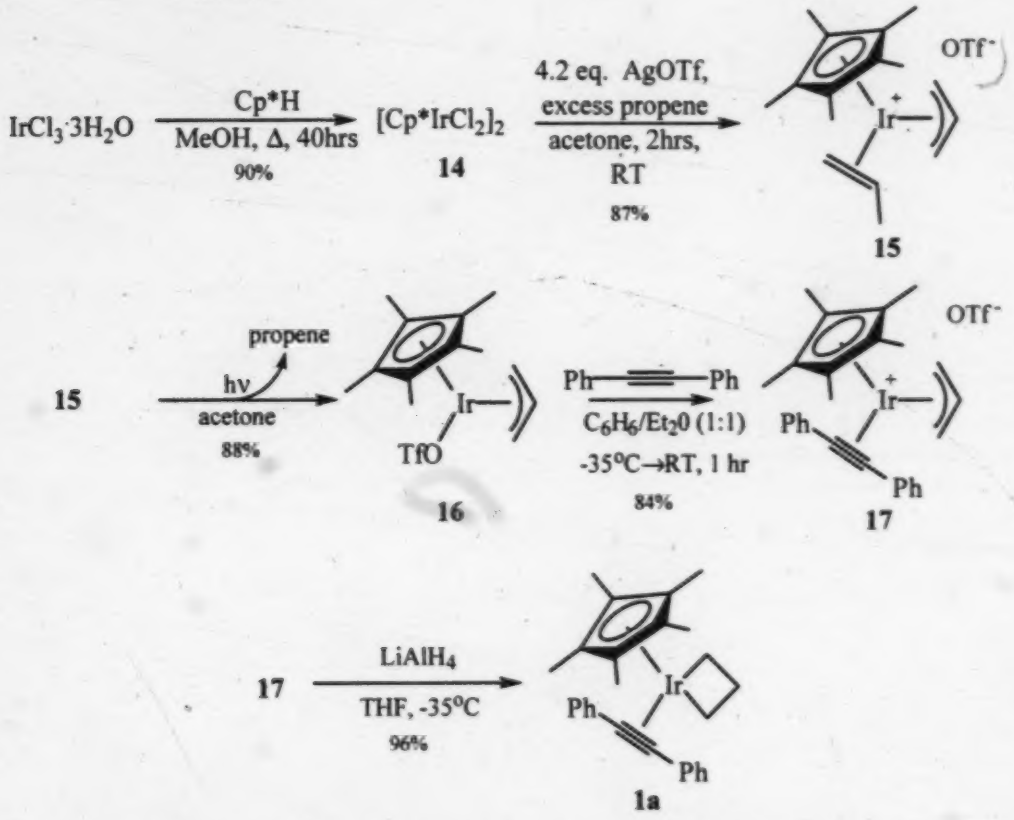
C. Results and Discussion

1) Synthesis of η^3-Allyl Alkyne Complex of Iridium

The synthetic route to the desired starting material was mostly established by Maitlis[58] and Schwiebert (Scheme 8).[35] However, the formation of the η^3-allyl alkyne complex **17** can be troublesome if Schwiebert's preparative procedure is strictly followed; it can result either in the formation of $[Cp^*Ir(\eta^5\text{-}C_5H_3Ph_2)]^+OTf^-$ and trace amounts of **17** (as determined by ^1H NMR spectroscopy)[32] or to unidentifiable decomposition products. Maitlis's procedure is used to make the allyl propene complex **15** from the commerically available iridium(III) chloride.[58] Photolysis of $Cp^*Ir(\eta^3\text{-allyl})$(propene) (**15**) in acetone labilizes the propene ligand while the triflate ion moves inner sphere to generate **16**. To isolate the allyl propyne complex **17** in high yield, a solution of **16** in benzene and diethyl ether is chilled to -35°C. A separate solution of diphenylacetylene was dissolved in diethyl ether, chilled to -35°C, and combined with the allyl complex **16** and stirred at room temperature to give a colorless precipitate, **17**, in 84% yield (see

Experimental section). The last step to form the parent metallacycle **1a** is nearly quantitative, as previously reported.[32]

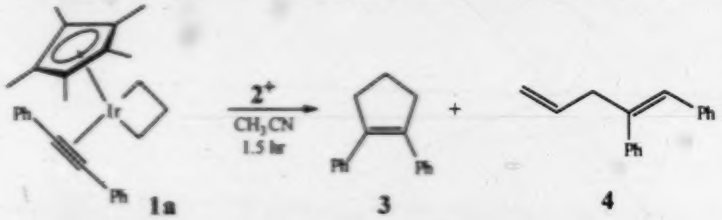
Scheme 8



2)Reactivity of the Parent Metallacycle with various oxidants/conditions

Since the basis for the oxidatively induced migratory insertion reactions was established using ferrocinium cations, we probed the reactivity of the iridacyclobutane alkyne complex **1a** with this oxidant, but in the presence of co-reductants to see if we could influence the equilibrium between the odd-electron (**III**) and the even-electron (**IV**) manifolds (Scheme 6). The reaction conditions were slightly modified from those of Schwiebert: typically, the reactions were initiated at 0 °C (to assist in giving high yields) and the oxidant with a PF_6^- counter ion was used.

Treating the parent metallacyclobutane complex **1** with excess of $Cp_2Fe^+BPh_4^-$ (**2a**$^+$, 2.4 equiv) in acetonitrile (0°C→room temperature) results in the formation of 1,2-diphenyl-cyclopentene **3**, in 68% yield (entry 1, Table 2). The yield of the cyclopentene **3** is 14% lower than the same reaction done by Schwiebert from 0°C→15°C, but it does



1a **3** **4** **(Eq. 9)**

Table 2: Results using various oxidants on reaction in Eq. 9.

Entry	ox./red.[a,b] (ratio)	temp(°C)	Product(s) (ratio)	Yield[d] (%)
1	**2a**$^+$	0→RT[c]	**3**	68
2	**2b**$^+$	0→RT	**3**	42-58[f]
3	**2c**$^+$	-35→RT	**3:4** (1:1)	69[e]
4	**2b**$^+$:**2d** (1:1)	0→RT	**3**	19-54[f]
5	**2b**$^+$:**2e** (1:1)	0→RT	**3**	31
6	**2b**$^+$:**2d** (2:1)	0→RT	**3**	45
7	**2b**$^+$:**2d** (1:2)	0→RT	**3**	40

[a] **2a**$^+$ = $Cp_2Fe^+BPh_4^-$; **2b**$^+$ = $Cp_2Fe^+PF_6^-$; **2c**$^+$ = $Cp'_2Fe^+PF_6^-$; **2d** = Cp_2Fe; **2e** = Cp'_2Fe. [b] Typically, 2.4 - 2.6 equivalents of the oxidant(ox.) or oxidant:reductant(red.) were used since optimum yields have been obtained with these amounts.[33] [c] RT = Room Temperature. [d] Yield determined by ^1H NMR spectroscopy. [e] Combined yield of organic products (33% of **3**; 36% of **4**). [f] Results from several independent experiments.

corroborate the earlier results.[33] Table 2 summarizes the results obtained for the oxidatively induced metal-mediated cycloaddition reaction (Eq. 9) using a variety of oxidants and oxidant/reductant pairs.

Althought altering the counter ion of the oxidant from **2a**$^+$ (BPh_4^-) to **2b**$^+$ (PF_6^-) was expected to give the same results as entry 1, a 10-26% drop in yield of the cyclopentene was observed (entry 2). This difference in reactivity of the two oxidants (**2a**$^+$ and **2b**$^+$) is not clear but we can suggest some plausible reasons. First, the purity of **2b**$^+$ may be questionable; this is echoed by Hendrickson and Duggan who also obtained the salt in "reasonably pure form."[93] Secondly, the presence of trace amounts of water, under certain conditions, could promote the partial solvolysis of the PF_6^- ion to the $PO_2F_2^-$ ion[91,92] especially in the presence of Lewis acids, despite the fact that many PF_6^- salts are made in water. Beyond these possibilities, the variablity in yields of the cyclopentene product **3** is a conundrum.

The only oxidant or oxidant/reductant combination to give any amount of diene **4** was the 1,1'-dimethylferricinium hexafluorophosphate (**2c**$^+$). By starting at -35°C and warming to room temperature, a 1:1 ratio of **3:4** (entry 3) was obtained, compared to the same reaction at room temperature, which gives a 1:2 ratio of **3:4**, respectively.[33] In this reaction, we propose that after the weaker oxidant (**2c**$^+$) oxidizes the iridacyclobutane complex, it becomes 1,1'-dimethylferrocene which behaves as a stronger reductant than ferrocene and favors the formation of **IV** (Scheme 6) at room temperature and ultimately generating the acyclic diene **4** (as discussed earlier). At -35°C, the partioning between the odd-electron manifold (**III**) and even-electron manifold (**IV**) appears to be almost equal, which would explain the nearly 1:1 ratio of products (**3:4**). It is noteworthy that the combined yield of organic products is 44% higher when the reaction is initiated at -35°C instead of at ambient temperature.[33] The lower total yield of products in the room temperature reaction could have been the result of faster decomposition of **2c**$^+$ in acetonitrile[33] or to increased control over the diene decomplexation (Scheme 6, **VII**→**4**).

Another interesting comparison can be made between the β-methyl-iridacyclobutane complex **1b** (Scheme 5) and the unsubstituted metallacycle complex (Table 2, entry 3). The reaction of complex **1b** with 1,1'-dimethylferricinium in

acetonitrile at room temperature gives the diene **11** exclusively in 40% yield whereas the reaction of the unsubstituted complex **1a** (at -35°C) returns the diene **4** and 1,2-diphenylcyclopentene in equal amounts. Clearly, oxidant $\mathbf{2c^+}$ favors the formation of the diene product.

We expected that the use of a reductant in combination with the oxidant would promote the formation of diene **4**; thus, after initial alkyne insertion, we proposed that the rate and extent of back reduction to the even-electron manifold (**IV**, Scheme 6) would be favored. However, the use of oxidant/reductant pairs generally decreased the yield of the cyclopentene product (**3**), but did not promote the formation of diene **4**. The 1:1 ratio of oxidant $\mathbf{2b^+}$ to reductant **2d** was troublesome and did not yield reproducible results (entry 4). Perhaps some of the problem is the occurance of competing redox reactions between the oxidant-reductant pair or the reaction of the oxidized metallacycle with the neutral metallacycle **1a**. The 1:1 ratio of oxidant/reductant pair $\mathbf{2b^+}$ and 1,1'-dimethylferrocene **2e** (entry 5) gave low yields (31%) of the cyclopentene product. When the ratio of oxidant ($Cp_2Fe^+PF_6^-$) to reductant (Cp_2Fe) was in either a 2:1 or 1:2 ratio (entry 6 and 7 respectively) yields ≥ 40% were observed for the exclusive formation of 1,2-diphenylcyclopentene. The lack of diene product is mystifying, but perhaps the added reductant prevents the oxidative diene decomplexation as proposed by Schweibert.[35]

One other problem with these reactions is with the oxidants themselves. Jordan's method of preparing the oxidants ($\mathbf{2a^+}$ = $Cp_2Fe^+BPh_4^-$; $\mathbf{2b^+}$ = $Cp_2Fe^+PF_6^-$; $\mathbf{2c^+}$ = $Cp'_2Fe^+PF_6^-$) is effective but the purification steps are not ideal.[94,95] Further, these oxidants (blue powders) are thermally sensitive.[93] A small amount of the corresponding ferrocene and/or decomposition products present (functioning as a reductant) can trigger a slow, catalytic redox reaction which can spoil the batch of oxidant to give large, orange-brown crystals (exactly how this occurs was not determined). For instance, when $\mathbf{2a^+}$ is dried at 40°C in a vacuum oven (at ~ 60 mm Hg) over 2 hours, rapid decomposition to a

black gummy residue occurred. Instead, the oxidants should be dried on the high vacuum line (10^{-5} Torr) at room temperature and then stored under nitrogen at -35°C.

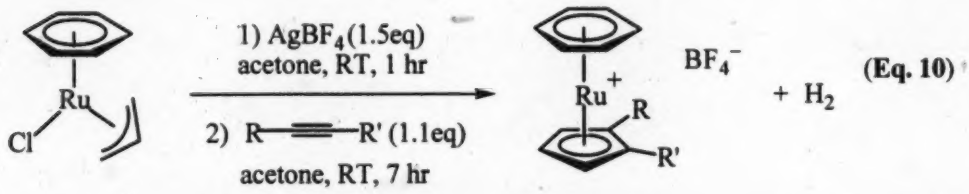
3)Summary

The otherwise unreactive iridacyclobutane complex is induced by a one-electron oxidation into a rich and complicated reactivity manifold where the distribution of products appears to be dependent upon a partitioning between odd and even-electron manifolds and by subtle reactivity differences on each energy surface. Even with this complexity, it seems that either manifold can be accessed selectively by the correct choice of oxidant and the correct choice of solvent.[33] The temperature at which the reaction occurs is also influential. The one electron oxidation reduces the kinetic barrier to alkyne migratory insertion and facilitates shifting the primary reactivity pattern of the resulting ring-expanded metallacycles from β-hydride elimination to reductive cyclization.

III. Synthetic Routes towards New $(L)_3Ru(\eta^3\text{-allyl})X$ Complexes

A. Introduction

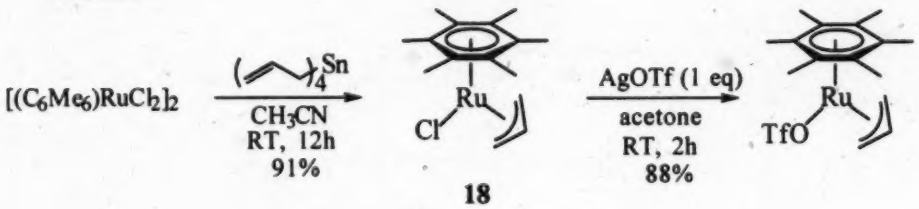
Rubezhov and coworkers first demonstrated that the reaction of $(\eta^6\text{-}C_6H_6)Ru(\eta^3\text{-allyl})Cl$ and silver tetrafluoroborate with an alkyne produces $(\eta^6\text{-benzene})Ru(\eta^5\text{-dialkylcyclopentadienyl})]^+BF_4^-$ complexes (Equation 10).[96] This reactivity is considered

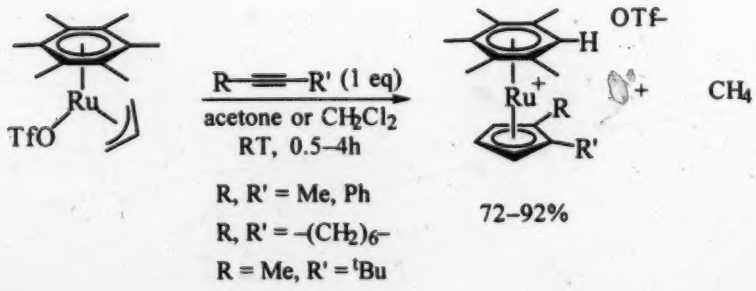


(Eq. 10)

to be a metal mediated [3+2] cycloaddition reaction that proceeds with loss of hydrogen. By introducing a larger and more electron rich aromatic ligand on the ruthenium, namely hexamethylbenzene, the analogous complex **18** was made in the Stryker group.[97] With this alteration of the template, an array of new cycloaddition chemistry has emerged, as illustrated in Schemes 9 and 10. These results will not be discussed in detail here, but

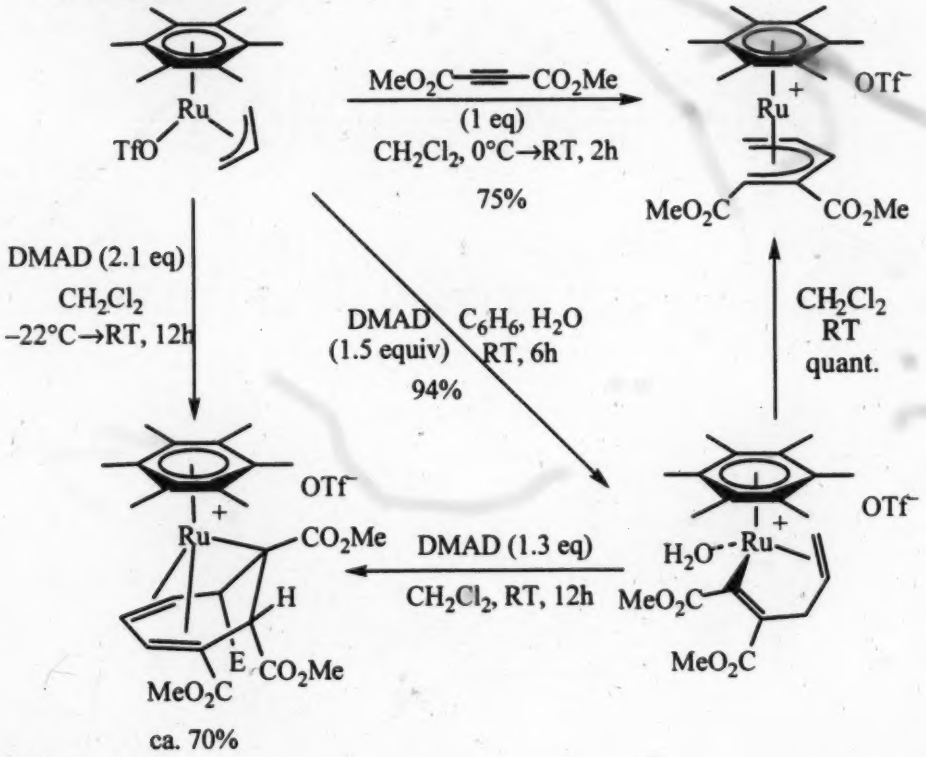
Scheme 9





both five and seven membered rings can be formed. The coordinated η^4,η^1-cycloheptadiene complex (Scheme 10) may not have formed a metal-carbon σ bond if the template had been more sterically encumbered. With this in mind, we wanted to develop a simpler template that could eventually be adapted into iron chemistry. In addition, we wanted to evaluate the effect of a stronger donor ligand set than the η^6-arene. This template should be better for functionalization and decomplexation of the seven membered ring with recovery of the metal.

Scheme 10



B. Project Goals

As a departure from the hexamethylbenzene ligand, we decided to look at other formally neutral 6-electron donor ligand systems in complexes of the form $(L_3)Ru(\eta^3$-allyl)X (where X = halide or triflate). These neutral "plates" (L_3) are η^6- analogues but

are really η^3 (or more precisely κ^3)[98] binding moieties, but with a much stronger donor character and a larger degree of steric bulk than the arene. Two ligand types were selected. The first ligand system targeted was the tris(pyrazolyl)methane (Tpm) class, including the tris(3,5-dimethylpyrazolyl)methane (Tpm*) ligand. The second ligand class was a tripodal phosphine, 1,1,1-tris(diphenyl-phosphinomethyl)ethane, which is known as triphos in some literature[99] but we prefer a moniker reflecting its structural backbone: tripod.

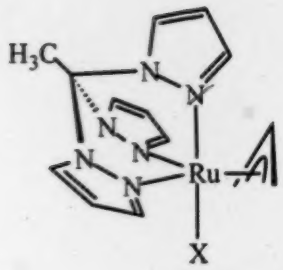
There have been hundreds of organometallic complexes constructed using tripod and over a hundred of these are ruthenium complexes.[100] Similarly, there are a few hundred organometallic complexes with either the Tpm or Tpm* ligand, about 80 of these being ruthenium complexes.[100] Despite the abundance of ruthenium complexes with these templates, we found that none of these complexes contained η^3-allyl ligands. This presented us with the unique challenge of constructing a new molecule.

C. Results and Discussion

1) Synthetic Attempts to (Tpm)Ru(η^3-allyl)X and (Tpm)Ru(η^3-allyl)X*

a) From (Tpm)RuX_3 or (Tpm)RuX_3*

Our initial strategy was to place the facially coordinating ligand Tpm or Tpm* on ruthenium(III) chloride and subsequently reduce this species to form a dimeric Ru(II) complex much like Bennett's dimer $[(C_6H_6)RuCl_2]_2$.[101] From this dimer, we planned to follow the same general synthetic route as Baird,[102] namely alkylation with tetraallyltin to form the targeted ruthenium allyl species, **19** (Figure 2).



X = halide, OTf

Figure 2: A target molecule (Tpm)Ru(η^3-allyl)X, **19**.

The known (Tpm)$RuCl_3$ complex **20** was prepared following Meyer's procedure (Eq. 11).[103] Successful dehydration of **20** was accomplished by heating at 100°C while

(Eq. 11)

20

under vacuum on the Schlenk line giving a quantiative amount of black, crystalline, anhydrous product, **20a** (no further purification was needed).

All attempts, varying temperature, concentrations, and molar quantities, to form the target η^3-allyl complex directly from either **20** or **20a** failed using typical allylating agents (eg. C_3H_5MgCl, tetraallyltin, allyltriphenyltin). For example, it was anticipated that reacting **20a** with excess Grignard could reduce the organometallic complex via an electron transfer process[1] while a second equivalent could allylate the Ru(II) complex to generate **19**.

Reducing complex **20a** using Na(Hg), Rieke Zn, Rieke Mg, triethylamine in ethanol[104] (or acetonitrile) did not form the anticipated $[(Tpm)RuCl_2]_2$, but instead gave

either paramagnetic material or indiscernible products. Even when (Tpm)$RuCl_3$ (**20a**) was reduced by Na/Hg in the presence of excess butadiene at -65°C→room temperature (in toluene), no discernible products were detected by ^1H NMR spectroscopy. To explain this last point, our intention was to use the Na(Hg) for the reduction of Ru(III) to Ru(0), occupy two coordination sites on the newly formed Ru(0) with the diene, and, in a subsequent step, protonate the diene to form an η^3-crotyl ($C_3H_4CH_3$) complex. Reacting either **20** or **20a** with any of the above reducing agents in the presence of allyl chloride gave only paramagnetic or intractable products. No effort was made to fully characterize the products in any of the reduction reactions. It is plausible that some kind of metal cluster is formed.

With the multitude of reactions indicating an unsuccessful approach to the target molecule, (Tpm)Ru(η^3-allyl)X, we turned our efforts to more indirect synthetic routes.

b) From (diene)Ru(allyl)$_2$

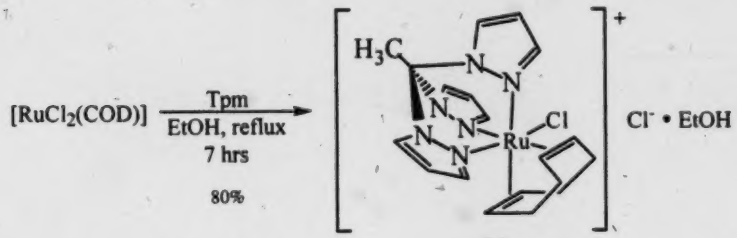
Since placing the neutral six-electron ligand on ruthenium followed by allylation did not give the target compound, we approached this synthetic problem by using a complex with the allyl ligand in place prior to replacing an existing chelating ligand. Thus, tris(pyrazolyl)methane was added to the known complexes bis(η^3-allyl)(1,5-cyclooctadiene)ruthenium(II) {(COD)Ru(η^3-allyl)$_2$ where COD = 1,5-cyclooctadiene} and the analogous norbornadiene (NBD) complex.[105,106] Treatment of (NBD)Ru(η^3-allyl)$_2$ or (COD)Ru(η^3-allyl)$_2$ with Tpm or Tpm* at reflux in acetonitrile, toluene, or xylenes only returned the starting materials. Similarly, photolysis of either (NBD)Ru(η^3-allyl)$_2$ or (COD)Ru(η^3-allyl)$_2$ with Tpm or Tpm* at in CH_2Cl_2 or CH_3CN yielded starting material.

Electrophilic attack by triphenylcarbenium cation (also known as trityl, Ph_3C^+) on one coordinated η^3-allyl ligand in either (COD)Ru(η^3-allyl)$_2$ or (NBD)Ru(η^3-allyl)$_2$ is known to abstract an allyl ligand to give [(diene)M(allyl)(S)$_2$]$^+X^-$ (where M=Ru(II) or

Os(II); S = solvent = acetonitrile; X = a pseudohalide).[107] The solvent ligands in these complexes can be readily displaced by a neutral chelating ligand.[107] However, treating the solvated ruthenium complex *in situ* with Tpm or Tpm* results in the formation of a mixture of green-yellow paramagnetic powder and allyltriphenylcarbenium, $Ph_3C(\eta^1$-allyl). This result indicates that electrophilic attack indeed occurs, but the exact composition of the powder is unknown. With this result, attention was directed to a complex that already had two ligands of the target molecule preformed.

c) From [(diene)Ru(Tpm)Cl]$^+$ Cl$^-$•EtOH

A literature method was used to construct [(Tpm)Ru(COD)Cl]$^+$Cl$^-$•EtOH (**21**) (Eq. 12).[108] We had anticipated that the reaction of **21** with allyl Grignard would



21 **(Eq. 12)**

exchange the inner sphere chloride, replacing it with an η^1-allyl ligand, and that heating would thermally displace the diene to allow for isomerization to the η^3-allyl. At that point, the outer sphere halide should move inner sphere producing the target compound **19**. All efforts of allylation (via C_3H_5MgCl, allyl chloride in refluxing ethanol, photolysis of allyl chloride in ethanol, photolysis of propene in ethanol) of **21**, however, proved to be ineffectual in synthesizing the target molecule.

2) Synthesis of (Tripod)Ru(η^3-allyl)X

With the Tpm target complex proving so elusive, attention was focused on a second template, which was also a facially coordinated ligand: tripod. Our goal was to construct $L_3Ru(\eta^3$-allyl)X where X = halide and L_3 is the bulky ligand 1,1,1-

tris(diphenylphosphinomethyl)ethane (tripod). A number of different synthetic routes were investigated; two independent routes were successfully developed.

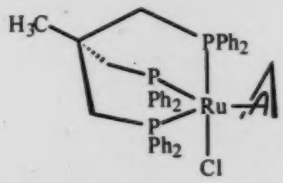


Figure 3: Target molecule of (tripod)Ru(η^3-allyl)Cl, **22**.

a) Direct Strategies

1) From [(tripod)Ru(μ-Cl)$_3$Ru(tripod)]$^+$ Cl$^-$ (**23**). Since this ruthenium dimer is readily available from the reaction of $RuCl_3 \cdot 3H_2O$ with tripod in ethanol at reflux, this material was prepared and subjected to typical allylating reagents and conditions. Under most conditions, however, no reaction was observed. On the occasions that a reaction did occur, one of the following conditions was employed, yet only intractable products were formed: i) allyltriphenyltin in benzene at reflux, ii) photolysis with propene in chloroform, iii) excess ethylene with 2 equiv. Na(Hg) in THF, iv) excess 1,3-butadiene with 2 equiv. Na(Hg) in THF, v) silver tetrafluoroborate in the presence of tetraallyltin. We surmise that the formation of this dimeric species is sterically inhibited enough not to give allylation even under harsh reaction conditions.

2) From (PPh$_3$)$_3$Ru(η^3-allyl)Cl (**24**). In 1970, Maxfield reported a convenient synthesis of trisphosphine complex **24**.* [111,113] We speculated that it might be possible to substitute the three triphenylphosphine ligands of (PPh$_3$)$_3$Ru(η^3-allyl)Cl with the tripod ligand to give the target compound, **22**. Heating complex **24** with tripod in benzene at reflux, however, leads only to decomposition while the same reaction at lower temperature or in different solvent returned only the starting material.

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* Maxfield only provided elemental analysis for this complex. We have further characterised **24** by ^{1}H, ^{13}C, and ^{31}P NMR spectrocopy; see experimental section. The X-ray crystal structure of this compound reveals a distored octahedral structure with a "vacant" site occupied by an α-hydrogen atom of one of the phenyl rings of the phospine ligand.[109-112]

3) From $RuCl_3 \cdot xH_2O$

The reaction of ruthenium trichloride and tripod with excess allylating reagents in various solvents gives uncharacterizable products. Only in the reaction of tetraallytin with these starting materials in a 1:1 benzene:THF solvent mixture at room temperature is a trace of the target compound **22** detected (by ^1H NMR spectroscopy) amongst an abundance of intractable materials. Recovery of this trace amount of material was thwarted by purification problems, chiefly the removal of tin residues.

b) Indirect Stategies

Since the direct routes do not lead to the target molecule, more indirect methods were pursued. Two of these routes lead to a synthesis of the target molecule, complex **22**.

1) From Ru_3CO_{12}, Thermal Route

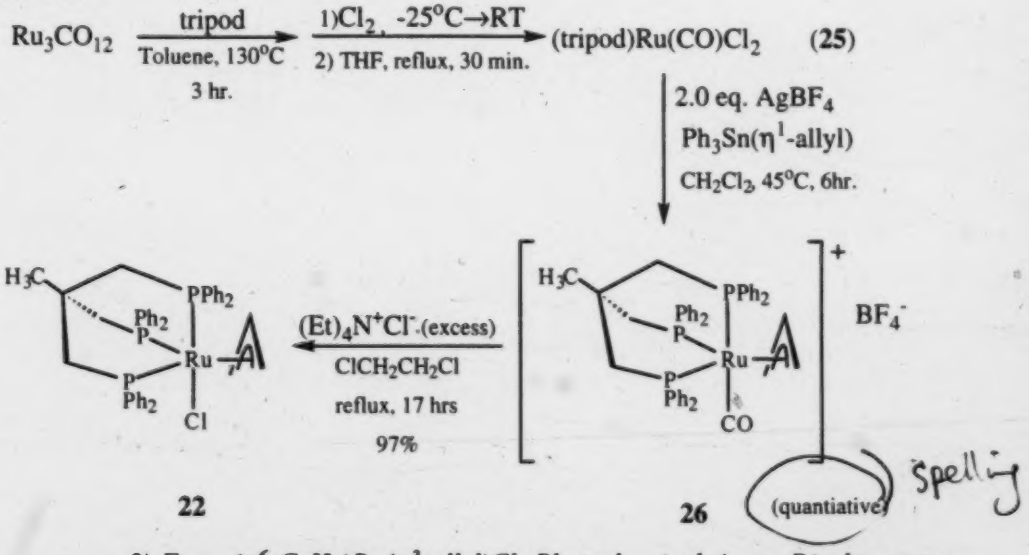
Instead of starting from initially oxidized ruthenium(III) such as ruthenium chloride, we developed an alternative strategy starting from the neutral metal in ruthenium dodecacarbonyl (Scheme 11). From this Ru(0) complex, all but one of the CO ligands dissociates and are replaced by tripod and two halide atoms to give **25** in 58% isolated yield upon thermolysis and oxidation with Cl_2 as previously reported by Collman (synthesis)[114] and Baird (spectroscopy).[99]

Direct allylation of complex **25** failed using Grignard reagents, tetraallyltin, or allyltriphenyltin. However, when complex **25** is treated with two equivalents of silver tetrafluoroborate in the presence of allyltriphenyltin in warm dichloromethane, cationic allyl complex **26** is formed in quantitative yield. By simply dissolving **26** in acetone in the presence of an excess of the respective sodium halide salts, the analogous chloride (**27**) and iodide (**28**) salts of **26** were made.[115] A strong absorption band in the IR spectrum was observed at 1997 cm^{-1} (CO stretch) for **26** and its salts. These results indicate that the carbon monoxide ligand is not labile under such mild reaction conditions.

Heating complex **26** to reflux in 1,2-dichloroethane facilitated CO loss while a chloride anion, provided by excess tetraethylammonium chloride, filled the vacant coordination site, forming (tripod)Ru(η^3-allyl)Cl, **22**, the desired target molecule. A low concentration (~ 2.9 x 10^{-3} mol/L) of **26** in 1,2-dichloroethane is essential in this reaction since at higher concentrations [(tripod)Ru(μ-Cl)$_3$Ru(tripod)]$^+$Cl$^-$ is readily formed as a by product. The reaction of **22** with $AgBF_4$ in acetone under CO pressure regenerates **26** cleanly.

The stereochemical orientation of the allyl ligand in complex **26** was not determined. It is evident, however, that the allyl can assume both *endo* and *exo* configurations, since there is a second set of allyl signals visible in the ^{1}H NMR spectrum of a sample left in solution (CD_2Cl_2) for several days.

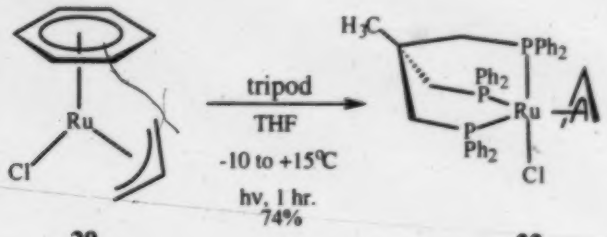
Scheme 11



2) From (η^6-C_6H_6)Ru(η^3-allyl)Cl, Photochemical Arene Displacement.

Since Bennett[101] and Baird[102] have shown that arene displacement in related complexes occurs photolytically, we also used this method to exchange benzene for tripod. A solution of (η^6-C_6H_6)Ru(η^3-allyl)Cl, **29**,[102,116] and tripod in anhydrous THF (and/or dichloromethane) was cooled to -10°C and photolyzed for 1 hour, giving the target

compound **22** in 74% isolated yield (Eq. 13).



29 **22** **(Eq. 13)**

Contrary to the photolytic lability of the *p*-cymene (*p*-$MeC_6H_4CHMe_2$) ligand that Bennett found with $[RuCl_2(p\text{-cymene})(PBu^n_3)]$,[93] this photochemical exchange reaction (Eq. 13) only works when the arene is benzene. Thus, photolysis of the *p*-cymene derivative analogous to **29** under the same conditions as those in equation 13 did not yield exchange. To further contrast and highlight the result shown in equation 13, Bennett attempted to photolytically exchange benzene in $[RuCl_2(C_6H_6)(PBu^n_3)]$ for *p*-cycmene but this returns the starting materials exclusively.[101]

Thermolysis of $[RuCl_2(C_6H_6)(PBu^n_3)]$ and hexamethylbenzene in heptane provided 15% exchange of arene.[101] Thermolysis of complex **29** with tripod in heptane at reflux for 24 hours however proved completely ineffective for arene exchange.

It is interesting to note that the allyl ligand in complex **29** has a dramatic influence on the photolytic displacement of benzene, sharply contrasting the lability of benzene observed in the reactions of $[RuCl_2(C_6H_6)(PBu^n_3)]$.

Although no mechanistic work has been done to probe how the arene is displaced, there are at least three feasible routes. One plausible rationale involves the allyl isomerizing from η^3 to η^1 to generate an initial open coordination site.[1,117-120] This would allow one of the electron donating phosphines of the tripod ligand to enter. Upon further photolysis, the arene ring could slip from η^6 to η^4 and open a second site for coordination of another phosphine "arm" of the tripod ligand. Subsequent slippage of the arene ring from η^4 to η^2 would open a third coordination site allowing for the third arm of

ligand isomerizing back to η^3, yielding the target molecule. However, a second mechanistic rationale does not involve allyl isomerization. Instead the arene displacement could proceed through a stepwise $\eta^6 \leftrightarrow \eta^4 \leftrightarrow \eta^2$ arene "unzipping" mechanism.[1,109] A third mechanistic rationalization involves an ionic dissociation of the chloride from the ruthenium; the open coordination site is occupied by solvent until initial phosphine coordination from the tripod ligand. After the initial phosphine coordination, a variety of possible rearrangements could occur but ultimately arene displacement would result and the halide would re-coordinate. The common theme in all these rationalizations is an initial event to generate an open coordination site.

It is interesting to note that there is some support for the ionic dissociation rationale since the photolysis is only effective when done in a polar solvent (CH_2Cl_2 or THF). However, this may also be due, in part, to the poor solubility of **29** in the nonpolar heptane.

We have found that the photolytic arene for tripod exchange reaction (Eq. 13) can proceed in as little as 35 minutes with a slight drop in isolated yield (67%). However, photolysis for times much longer than 1.5 hours results in the formation of the dimeric ruthenium complex, $[(tripod)Ru(\mu\text{-}Cl)_3Ru(tripod)]^+Cl^-$, by an unknown reaction mechanism.

3) Spectroscopy of (tripod)Ru(η^3-allyl)Cl, 22

At room temperature, the proton NMR of (tripod)Ru(η^3-allyl)Cl shows an underlying broad hump 6.5-7.9 ppm among three more distinctive aromatic resonances. We suspected that the broadness could be attributed to one of the arms of the tripod ligand dissociating and rapidily reconnecting with the metal center. The charaterization of complex **22** is more clearly defined in this region when the sample is chilled to -80 °C (see experimental section). This results in four distinct aromatic resonances, however, the 6.90-7.55 ppm region of the ^1H NMR spectrum is still quite complex.

experimental section). This results in four distinct aromatic resonances, however, the 6.90-7.55 ppm region of the ^{1}H NMR spectrum is still quite complex.

Examining the $^{31}P[^{1}H]$ spectrum at various temperatures was useful in characterising this fluxional behavior (see Figure 4). At 30 °C, broad multiplets are observed for both the apical and the equatorial phosphines. At lower temperatures, this fluxionality slows and becomes very slow at -60 °C. These results are consistent with a fluxional process and explains the broad peaks observed in the ^{1}H NMR spectrum.

While the temperature was maintained at -80 °C, the apical phosphorus atom was irradiated (48 ppm) and the ^{1}H NMR spectrum was recorded. This gave rise to the collapse of the triplet at 6.33 ppm (normally observed without ^{31}P coupling) to a doublet. This signal is clearly due to an ortho proton of a phenyl ring bonded to the apical phosphorus atom. A second discrete resonance occurs for the apical methylene protons (2.03 ppm) which had collapsed from a doublet at -80 °C (without ^{31}P decoupling) to a singlet at -80 °C with ^{31}P decoupling.

The ^{1}H NMR spectrum was also recorded at -80 °C while the "equatorial" phosphorus at 18 ppm was irradiated; the changes relative to the spectrum without phosphorus decoupling are subtle. The broad singlet at 7.72 ppm (without ^{31}P decoupling) becomes a broad multiplet and the aromatic region from 6.90-7.55 ppm becomes partially resolved under these conditions. In contrast to their sharp peaks at ambient temperature, the terminal protons of the allyl ligand, the H_a and H_s protons (3.30 ppm and 2.86 ppm, respectively) were observed to have a weak coupling to phosphorus as these peaks are slightly broad at -80 °C without ^{31}P decoupling; however, no coupling constant was resolved. The terminal allyl proton peaks became sharpened with ^{31}P decoupling at -80 °C which supports the proposed tripod fluxionality. Sharpening of the tripod methylene protons at 2.43 ppm with ^{31}P irradiation at 18 ppm provided the most supportive evidence of their "equatorial" orientation when compared to the non-irradiated ^{1}H NMR spectrum.

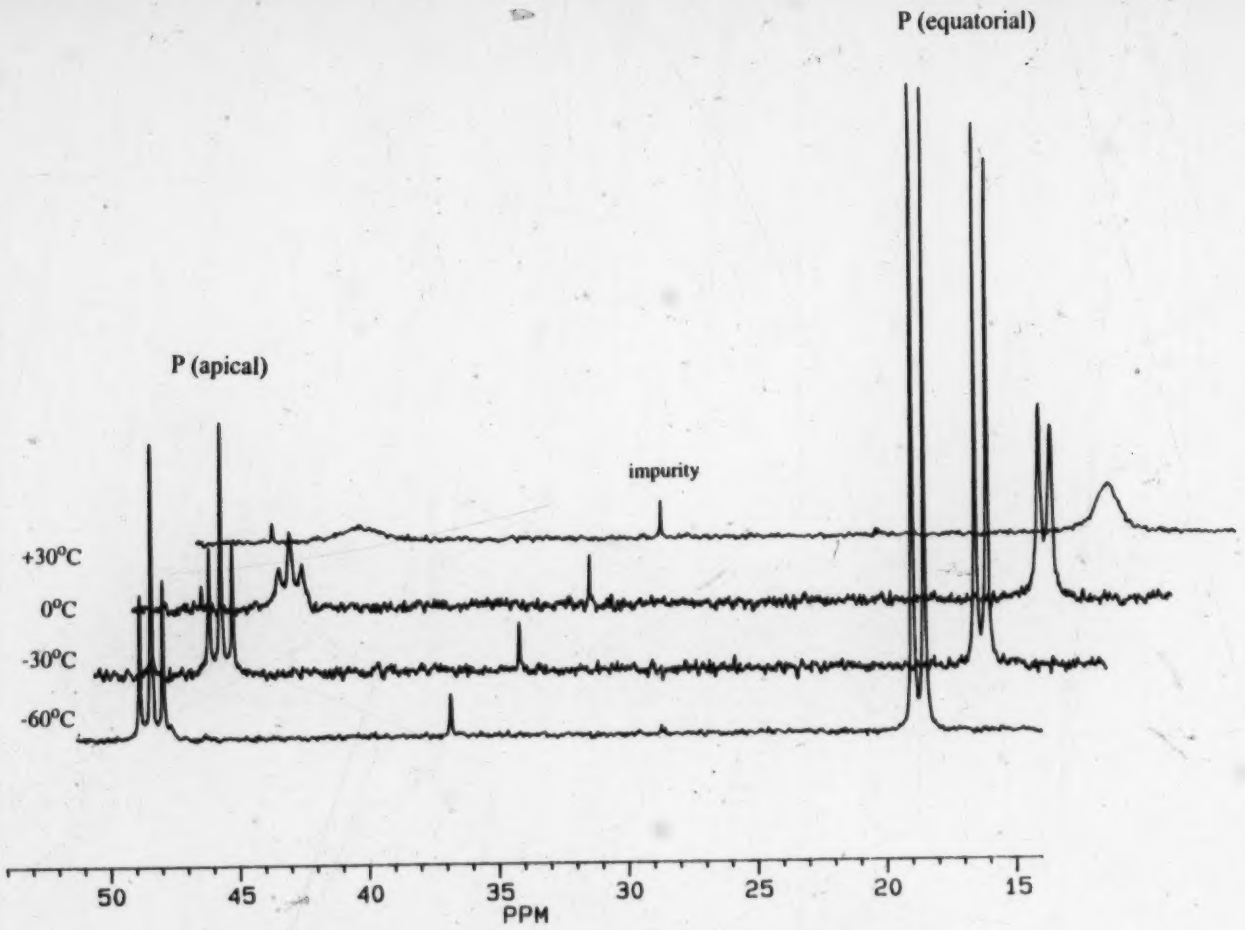


Figure 4: $^{31}P[^{1}H]$ Variable Temperature NMR of **22** at 81 MHz.
(Spectra are offset; δ = 48 ppm P(apical), δ = 18 ppm P(equatorial).)

With this information, we attempted to assign the aromatic region of the ^1H NMR spectrum of **22**. Since the limit of resolution of the aromatic region was essentially reached at -40°C, selective proton decoupling experiments were conducted at this temperature. These spectra were futher simplified by broadband ^{31}P decoupling;

Table 3: Correlation of Phenyl Rings of **22** by $^1H\{^{31}P\}$ NMR at -40°C on the 400 MHz instrument.

Blank[a] → *Inference*	7.72 d *J*=7.0 Hz	7.43 d *J*=7.2 Hz	7.25-7.38 *m*	7.16 t *J*=7.4 Hz	6.98-7.08 *m*	6.75 t *J*=7.6 Hz	6.38 d *J*=7.6 Hz
H_o Ring1	d	d	m	t	m	**d**[b]	*Irradiate*
H_m Ring1	d	d	m	t	**m** (SA)[c]	*Irradiate*	**s**
Hp Ring1[d] *and* *H_m Ring2*	***d***	**s**	m	**s**	*Irradiate* *7.03 ppm*	**d**	d
Hp Ring2[d]	d	d	m	*Irradiate*	**m** (SA)	d	d
Hp; H_m Ring3	**s**	d	*Irradiate*	t	m	t	d
H_o Ring2	d	*Irradiate*	m	t	**m** (SA)	t	d
H_o Ring3	*Irradiate*	d	**m** (SA)	t	m	t	d

[a]This spectrum was recorded without any other protons simultaneously irradiated; chemical shifts are in ppm. [b]Bold type = highlights change from blank[a]. (SA)[c] = multiplet peak shape altered from blank[a]. [d]The differing horizontal levels indicate resonances from different aromatic rings in cases where there could be some confusion.

the results are given in Table 3. When correlated with the data above, this work

(which lie in the equatorial plane) of the equatorial phosphine atoms can shield the protons of Ring 1 (Figure 5). The assignment of phenyl protons on the equatorial

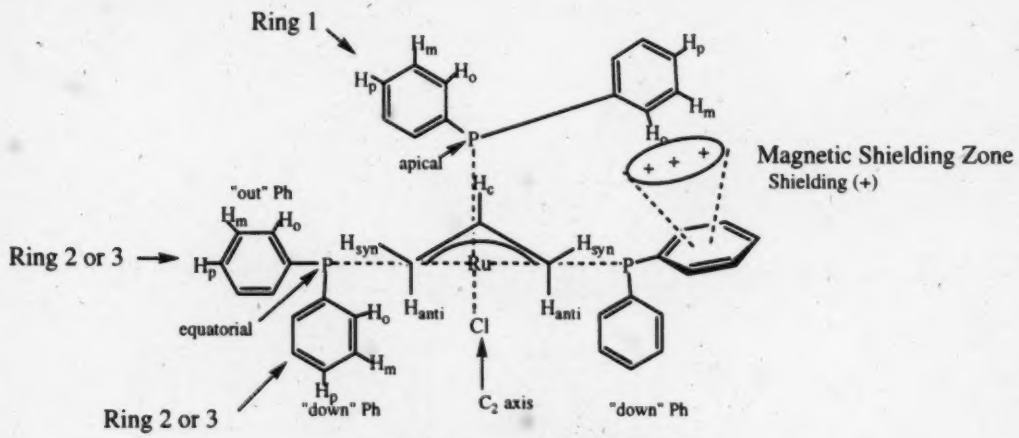


Figure 5: Labeling and rationalizing aromatic protons of **22**.

phosphine atoms was accomplished with the experiments in Table 3, however, the assignment as to which aromatic ring is in what orientation ("out" or "down") remains unclear.

4) Reactivity of Ruthenium(η^3-allyl) Complexes.

In our quest for seven-membered carbocyclic rings, we explored the reactivity of [(tripod)Ru(η^3-allyl)CO]$^+BF_4^-$ (**26**) in dichloromethane with each of DMAD, diphenylacetylene, phenylacetylene, and 1-butyne. In all cases, starting material was returned.

In dichloromethane, exploratory work was also performed with Maxfield's compound, $(PPh_3)_3Ru(\eta^3\text{-allyl})Cl$ (**24**)[113] to probe its reactivity with alkynes (DMAD, diphenylacetylene, and 2-butyne), however, these were only successful at generating intractable materials.

diphenylacetylene, and 2-butyne), however, these were only successful at generating intractable materials.

Since seven-membered carbocyclic rings have been formed by the reaction of DMAD with **18**[95] in trifluoroethanol, which assists in the generation of ionic species, we too began our exploratory reactivity of **22** with alkynes in this solvent. Unfortunately, we found that this solvent was too acidic and led to the formation of [(tripod)Ru(μ-Cl)$_3$Ru(tripod)]$^+$Cl$^-$ (**23**) and other intractable products. Other results indicate that acetone and dichloromethane are preferred solvents for **22**.

On a slightly more successful note, the (tripod)Ru(η^3-allyl)Cl (**22**) does display some reactivity. Preliminary experiments of cations and/or complexes derived from the treatment of **22** with DMAD and diphenylacetylene in CH_2Cl_2 indicate the disappearance of allyl peaks and the formation of new compounds. Work is currently underway to characterize these. Preliminary screening experiments of the reactivity of **22** with other alkynes (phenylacetylene, 2-butyne, 3-butyn-1-ol) have provided intractable materials. Further experiments are necessary to probe the scope of reactivity of this new complex.

IV. Conclusions

We have confirmed some of the reactivity patterns of oxidatively induced cyclization of [Cp*Ir(η^3-allyl)(PhC≡CPh)] as noted earlier by Schwiebert.[35] In addition, we have modified conditions slightly to find that there are some subtleties, such as a temperature dependence, that are not well understood. The addition of a conjugate reductant of the oxidant seems only to serve as a poison for the oxidant and results in low yield of the cyclopentene product.

In the second part of the project, we found that creating the target molecule,[(tripod)Ru(η^3-allyl)Cl] (**22**), was difficult using simple approaches. During the search for the target molecule, we have also prepared [(tripod)Ru(η^3-allyl)CO]$^+BF_4^-$ (**26**). Preliminary experiments of **26** with alkynes indicate no reactivity; nevertheless, **22** is reactive. Further investigations are required to fully probe both the reactivity and products obtained when **22** is reacted with a host of alkynes under various conditions.

V. Experimental Section

1. General: All reactions, unless otherwise specified, were performed under a nitrogen atmosphere in an MBraun Lab Master 100 dry box or using a dual manifold vacuum/nitrogen line and common Schlenk techniques; vacuum was obtained using a two-stage mechanical pump (10^{-3} Torr) and ultra pure ($\leq$ 1 ppm O_2) nitrogen was used as received. The dry box atmosphere was maintained below 1 ppm O_2 and the box was equipped with a freezer which was maintained at -35°C. Thermolysis of solutions at temperatures greater than the boiling point of the solvent was performed by sealing the degassed solution in a glass tube and submerging the reaction vessel into a sand bath up to the neck of the flask. Reactions requiring greater than atmospheric pressure were carried out in reactors consisting of a thick-walled glass Fisher-Porter bottle, available from Andrews Glass Company, fitted with a safety pressure release valve, a sample withdrawal port, and a quick connect hookup.[121] Photolysis reactions were performed using a Hanova 450 Watt lamp and Pyrex filters.

Infrared (IR) spectra were recorded on a Nicolet 250 or 7199 Fourier transform spectrophotometer and are reported in reciprocal wave numbers (cm^{-1}) and calibrated with the 1601 cm^{-1} absorption of polystyrene. Nuclear magnetic resonance (NMR) spectra were recorded on Varian 300i (^1H, 300 MHz), Bruker AM-300 (^1H, 300 MHz; ^{13}C, 75 MHz), Bruker AM-360 (^1H, 360 MHz), and Bruker AM-200 (^1H, 200 MHz; ^{13}C, 50 MHz; ^{31}P, 81.1 MHz) spectrometers, using long relaxation delay times to optimize peak integrals for determination of yields using internal standards. Chemical shifts are reported in ppm relative to TMS (^1H and ^{13}C NMR spectroscopy) or H_3PO_4 (^{31}P NMR spectroscopy). Mass spectra were obtained on either a Kratos MS50 mass spectrometer operating at 70 eV (10,000 Resolution) for electron impact (EI) or on a MicroMass ZabSpec oATOF for electrospray (Resolution = 1,000 for low resolution;

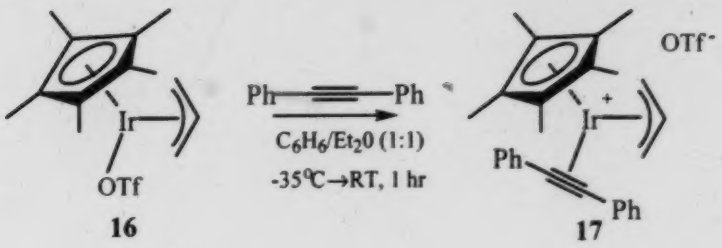
10,000 for high resolution). Elemental analyses were performed by the University of Alberta Microanalysis Laboratory.

Special NMR Experiments: The correlation NMR spectoscopy techniques of GCOSY, HMQC, and NOE experiments are described elsewhere.[122-126] Some ^{13}C NMR spectra were obtained using the pulse sequence traditionally designated as the "attatched proton test" (APT) which provides information similar to that obtained by DEPT experiments.[127,128]

Atom Labels for Spectroscopic Data: The protons on allyl ligand are referred to as H_c (central), H_s or H_{syn} (*syn* with respect to the central proton), and H_a or H_{anti} (*anti* with respect to the central proton). The allyl carbon atoms are labeled C_t (terminal carbon) and C_c (central carbon).

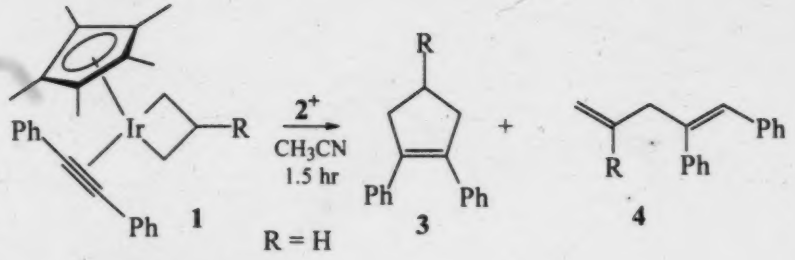
Materials: Unless indicated otherwise, solvents and reagents were purchased from commercial vendors and used as received. Benzene, hexanes, pentane, tetrahydrofuran, and diethyl ether were purified by distillation from sodium benzophenone ketyl. Dichloromethane was distilled from calcium hydride. Acetonitrile were distilled from calcium hydride and deoxygenated by three freeze-pump-thaw cycles if this solvent was to be used inside the dry box. Celite filtrations were performed using a plug of Hyflo Super Cel (Fisher) over glass wool in disposal pipettes or alone on fritted glass funnels under vacuum. The following compounds were prepared as described in the literature: $[Cp^*Ir(\eta^3\text{-}C_3H_5)(PhC{\equiv}CPh)]$ (**1**),[35] $Cp_2Fe^+BPh_4^-$ (**2a**$^+$),[94,95] $Cp_2Fe^+PF_6^-$ (**2b**$^+$),[94,95] $Cp'_2Fe^+PF_6^-$ (**2c**$^+$),[94,95] $[Cp^*Ir(\eta^3\text{-}C_3H_5)(\eta^2\text{-}C_3H_6)]$ (**15**),[58] $[Cp^*Ir(\eta^3\text{-}C_3H_5)OTf]$ (**16**)[35] $[TpmRuCl_3]{\bullet}1.5H_2O$ (**20**),[103] $[(COD)Ru(\eta^3\text{-}C_3H_5)_2]$,[105,106] $[(NBD)Ru(\eta^3\text{-}C_3H_5)_2]$,[105,106] $[(COD)Ru(Tpm)Cl]^+Cl^-{\bullet}EtOH$ (**21**),[108] $[CH_3C(CH_2PPh_2)_3]$ = tripod,[49]

[(tripod)Ru(μ-Cl)$_3$Ru(tripod)]$^+$Cl$^-$ (**23**),[129] (PPh$_3$)$_3$Ru(η^3-allyl)Cl (**24**),[113] [(tripod)RuCl$_2$(CO)] (**25**),[114] [(η^6-benzene)Ru(η^3-C$_3$H$_5$)Cl] (**29**).[102,116]



16 **17**

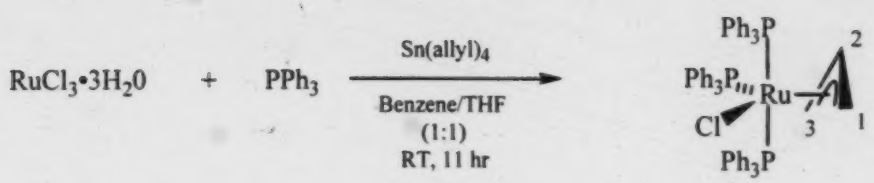
[Cp*Ir(η^3-C_3H_5)(PhC≡CPh)]$^+$OTf$^-$ (17): (Modification of Schwiebert's method[35]) In the dry box, 25.1 mg (0.0485 mmol) of allyl triflate, **16**, was placed in a 3 dram vial (with stir bar) with 2 mL benzene and 2 mL diethyl ether; the solution was placed into the -35°C freezer for 20 minutes. In a separate 1 dram vial, 14.5 mg (0.0814 mmol) of diphenylacetylene was dissolved in 1 mL diethyl ether and placed in -35°C freezer for 10 minutes. The chilled solutions were combined, turning cloudy white initially, and stirred at room temperature for 1 hour. A white precipitate formed. The orange solution was removed with a pipette and discarded. The product was rinsed with several portions of Et_2O and then dried under vacuum overnight. This gave 28.4 mg (0.0408 mmol, 84.1%) of **17**, which was spectroscopically identical to that obtained by Schwiebert.[35]



Oxidatively Induced Reactions.

The following proceedure was generally used for all oxidatively induced reactions but will differ for the amount and types of oxidants and reductants used, the temperatures, and the reaction times (see Table 2 in the results and discussion section). An internal standard of 3,3'-bianisole (3,3'-dimethoxybiphenyl) was used for comparitive purposes when integrating the peaks in the ^1H NMR spectra.

In the drybox, a solution of 8.9 mg (0.016 mmol) of **1** in $CDCl_3$ was mixed with 2.0 mg (0.0093 mmol) of 3,3'-bianisole (3,3'-dimethoxybiphenyl). A base line (time 0) ^1H NMR spectrum was taken of this sample. The sample was taken back in the drybox and transfered to a small Schlenk bomb; the solvent was then removed *in vacuo*. Approximately 0.5 mL acetonitrile was added to this bomb and sealed. The bomb was removed from the drybox, placed on the Schlenk line and cooled to 0 °C. Under a strong nitrogen purge, all of the dry, solid oxidant 21.5 mg (0.0425 mmol) of $Cp_2Fe^+BPh_4^-$ (**2a**$^+$) was added into the bomb in one portion. The sealed vessel was kept at 0 °C for 40 minutes, then warmed to ambient temperature for 45 minutes. The solvent was removed *in vacuo*. The vessel was taken back into the drybox where the residue was taken up in $CDCl_3$, filtered through a pad of Celite, and placed in an NMR tube. The ^1H NMR spectrum was recorded (time "1.5 h"). The result was the cyclopentene product **3** as determined by comparison of the ratio of bianisole to metallacycle (at time 0) with the ratio of bianisole to the reaction products (at time 1.5 h).



24

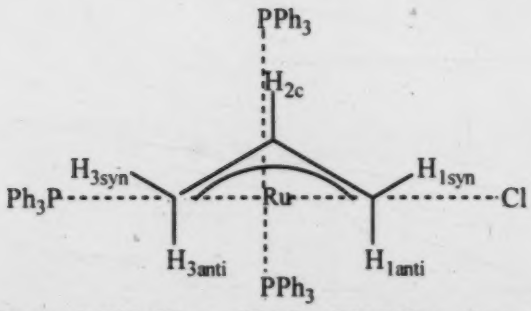
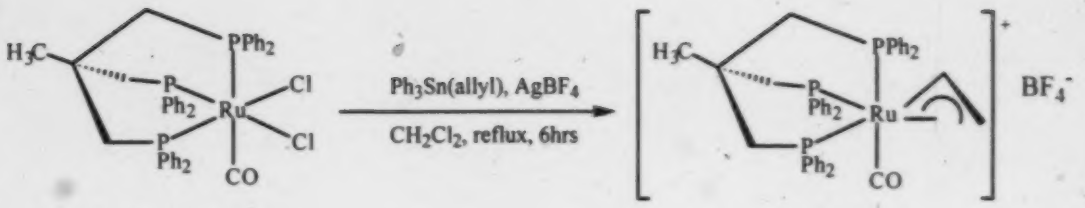


Figure 6: Side View of **24** for 1H NMR assignments.

$(PPh_3)_3Ru(\eta^3$-allyl)Cl (24): Although Maxfield reported the synthesis of this molecule, only an elemental analysis was provided.[113] The following spectroscopic assignments are tentative; based on the premise that one arene ring is shielding the proximal end of the allyl ligand: the H_{syn2}, H_{anti2} allyl protons (see Figure 6). ^1H NMR (300 MHz, $CDCl_3$) δ 7.35-6.67 (complex multiplets, 45H, aromatic), 4.16-4.39 (m, 1H, H_{2c}), 2.69 (m, 1H, H_{1syn}), 1.74 (m, 1H, H_{3syn}), 0.65 (dd, 1H, J = 12.6, 10.1 Hz, H_{1anti}), 0.41 (m, 1H, H_{3anti}); ^{31}P NMR (81.1 MHz, $CDCl_3$) δ 81.02; $^1H[^{31}P]$ NMR (300 MHz, $CDCl_3$) δ 7.35-6.67 (m, 45H, aromatic), 4.35 (dddd,[130] 1H, $J_{H2c\text{-}H1anti}$ = 10.0 Hz; $J_{H2c\text{-}H3anti}$ = 9.5 Hz; $J_{H2c\text{-}H1syn}$ = 6.5 Hz; $J_{H2c\text{-}H3syn}$ = 6.5 Hz, H_{2c}), 2.72 (d, 1H, $J_{H1syn\text{-}H2c}$ = 6.5 Hz, H_{1syn}), 1.76 (d, 1H, $J_{H3syn\text{-}H2c}$= 6.5 Hz, H_{3syn}), 0.68 (d, 1H, $J_{H1anti\text{-}H2c}$ = 10.0 Hz, H_{1anti}), 0.44 (d, 1H, $J_{H3anti\text{-}H2c}$ = 9.5 Hz, H_{3anti}); $^1H[^{31}P$; ^1Hc (4.35 ppm)] NMR (300 MHz, $CDCl_3$) δ 2.72 (s, 1H, H_{1syn}), 1.76 (s, 1H, H_{3syn}), 0.68 (s, 1H, H_{1anti}), 0.44 (s, 1H, H_{3anti}); ^{13}C NMR APT(75 MHz, $CDCl_3$) δ 127.38-128.11 (aromatic), 77.94 (C_2), 56.87 (C_3), 46.92 (C_1); Analysis calc'd for $C_{57}H_{50}P_3ClRu$: C, 70.98; H, 5.23; found: C, 70.99; H, 5.35 %.



25 **26**

[(tripod)Ru(η³-allyl)(CO)]⁺BF_4^- (26). In the dry box, a 50 mL Schlenk flask was charged with (Tripod)Ru(Cl)$_2$(CO)[114] (1.5191 g, 1.8421 mmol), allyltriphenyltin (0.8703 g, 2.2254 mmol, 1.2 equiv), silver tetrafluoroborate (0.7887 g, 4.0513 mmol, 2.2 equiv) and capped with a rubber septum. The flask was taken outside the dry box where 15mL of reagent grade dichloromethane was injected. Under a purge of nitrogen, a condenser was placed on to this flask. The solution was stirred and brought to reflux (45°C). The solution began to turn purple after a few minutes. After six hours at reflux, the solution was cooled to room temperature. The material was filtered (in air) through a pad of Celite to remove the silver salts. The solvent was removed *in vacuo* to give a white solid. The solid was triturated first with hexanes, then with ether, and lastly with toluene to remove tin residues. Residual solvents were removed *in vacuo* to give 1.6242 g (1.8422 mmol, quantitative) of spectroscopically pure (by ^{1}H NMR) **26**.

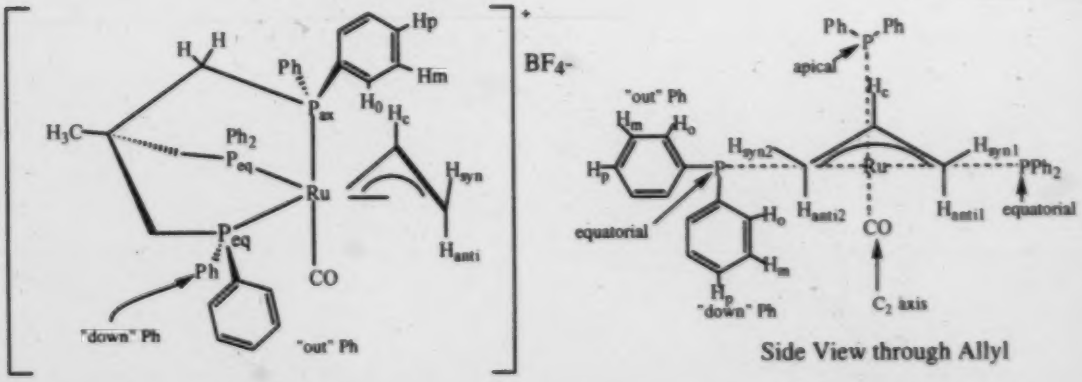
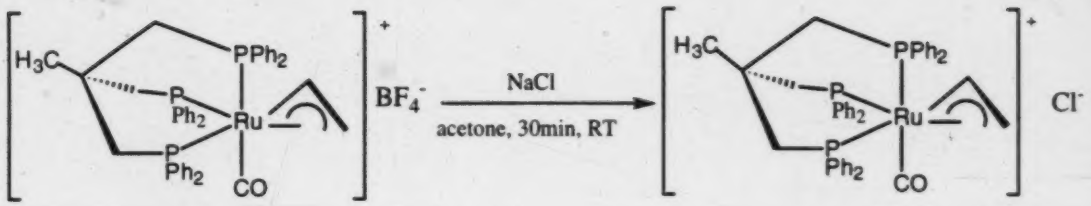


Figure 7: Labeling Scheme for Spectroscopic Assignments of Complex **26**.

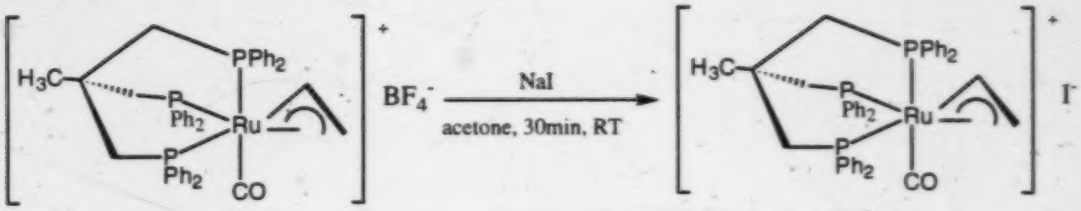
IR (KBr, $CDCl_3$, cast, cm^{-1}): 3062 (w), 1996 (s, CO), 1483 (w), 1434 (s), 1092 (s), 1055 (vs, C-O stretch), 999 (m), 832 (w), 730 (s), 697 (vs), 585 (w), 544 (m), 517 (s), 482 (w), 451 (w); ^{1}H NMR (300 MHz, acetone-d_6) δ 7.75-7.78 (m, 4H, aromatic), 7.18-7.48 (m, 18H, aromatic), 6.98 (td, 4H, aromatic, J = 7.5, 2.4 Hz), 6.60 (apparent t, 4H, $J_{apparent}$ = 9.3 Hz, aromatic), 4.94 (m, 1H, H_c), 2.91-3.09 (m, 6H, CH_2, equat. of tripod, H_{anti} of allyl), 2.77 (d, 2H, J = 7.1 Hz, H_{syn}), 2.58 (d, 2H, $^2J_{P(ax)-H}$ = 9.4 Hz,CH_2, axial of tripod), 1.89 (q, 3H, $^4J_{P-H}$ = 3.2 Hz); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.52-7.61 (m, 4H, aromatic), 7.17-7.40 (m, 18H, aromatic), 6.92 (td, 4H, aromatic, J = 7.9, 2.2 Hz), 6.46 (apparent t, 4H, $J_{observered}$ = 9.3 Hz, Ho axial), 4.83 (m, 1H, H_c), 2.83-2.91 (m, 2H, H_{anti}) 2.66-2.76 (m, 6H, CH_2 of tripod), 2.43 (d, 2H, $J_{H_{syn}-H_c}$ = 9.4 Hz, H_{syn}), 1.86 (d, 3H, $^4J_{P-H}$ = 3.1 Hz, CH_3 of tripod); ^{13}C[^{31}P; ^{1}H] (50 MHz, acetone-d_6) δ 138.65 ($C_{quat.}$, aromatic), 138.03 ($C_{quat.}$, aromatic), 132.84 (CH_o, axial), 132.45 (CH), 132.11 (CH), 131.25 (CH_p, axial), 131.12 (CH), 130.80 (CH), 129.71 (CH), 129.48 (CH), 129.26 (CH_m, axial), 95.96 (CH, central of allyl), 46.92 (CH_2, terminus of allyl), 38.36 ($C_{quat.}$, tripod), 37.59 (CH_3, tripod), 34.77 (CH_2, apical of tripod), 33.48 (CH_2, equatorial of tripod); ^{13}C[^{1}H] (75 MHz, acetone-d_6) δ 139.00 (s, $C_{quat.}$, aromatic), 138.39 (s, $C_{quat.}$, aromatic), 137.75 (s, $C_{quat.}$, aromatic), 132.86 (d, $^2J_{C-P}$ = 9.7 Hz, CH_o, axial), 132.44 (t, $^2J_{C-P}$ = 5.6 Hz, CH_o, aromatic), 132.15 (t, $^2J_{C-P}$ = 5.2 Hz, CH_o, aromatic), 131.27 (s, CH_p, axial), 131.14 (s, CH_p, aromatic), 130.82 (s, CH_p, aromatic), 129.74 (t, $^3J_{C-P}$ = 5.0 Hz, CH_m, aromatic), 129.50 (t, $^3J_{C-P}$ = 4.9 Hz, CH_m, aromatic), 129.29 (d, $^2J_{C-P}$ = 9.6 Hz, CH_m, axial), 95.99 (s, CH, central of allyl), 46.96 (t, J = 7.4 Hz, CH_2, terminus of allyl), 38.40 (d, $^2J_{C-P}$ = 3.4 Hz, $C_{quat.}$, tripod), 37.63 (q, J = 10.4 Hz, CH_3), 34.83 (d, $^1J_{C-P}$ = 24.5 Hz, CH_2, apical of tripod), 33.52 (dd, $^1J_{C-P}$ = 29.2 Hz, 4.9 Hz, CH_2, equatorial of tripod); ^{31}P[^{1}H] (81 MHz, acetone-d_6) δ 18.85 (dd, 2P, $^2J_{eq1-ax}$ = 46.2 Hz, $^2J_{eq2-ax}$ = 40.6 Hz, P_{eq}), 14.62 (dd, 1P, $^2J_{ax-eq1}$ = 46.2 Hz, $^2J_{ax-eq2}$ = 40.6 Hz, P_{ax}); HMQC (300MHz, acetone-d_6) δ 1.89 (CH_3) ↔ δ 37.59 (CH_3), δ 2.58 (H_{anti}) ↔ δ

34.77 (CH_2, apical), δ 2.77 (H_{syn}) ↔ δ 46.92 (CH_{syn}), δ 2.92-3.09 (CH_2; H_{anti}) ↔ δ 33.48-38.36 (CH_2, equatorial of tripod; CH_{anti}), δ 4.94 (H_c) ↔ δ 95.96 (CH_c), δ 6.60 (H_o) ↔ δ 132.84 (CH_o, axial), δ 6.98 (H, aromatic) ↔ δ 129.26-129.71 (CH, aromatic), δ 7.18-7.48 (H, aromatic) ↔ δ 130.80-131.25 (CH, aromatic), δ 7.75-7.78 (H, aromatic) ↔ δ 132.11-132.45 (CH, aromatic); GCOSY (300MHz, acetone-d_6) allyl ligand only δ 2.77 (H_{syn}) ↔ δ 3.00 (H_{anti}), δ 3.00 (H_{anti}) ↔ δ 4.94 (H_c); Mass Spec (electrospray, +ve,): *m/z* 795 $[M\text{-}BF_4]^+$, 767 $[M\text{-}BF_4,CO]^+$. An analytically pure sample could not be obtained despite repeated attempts at recrystallization.



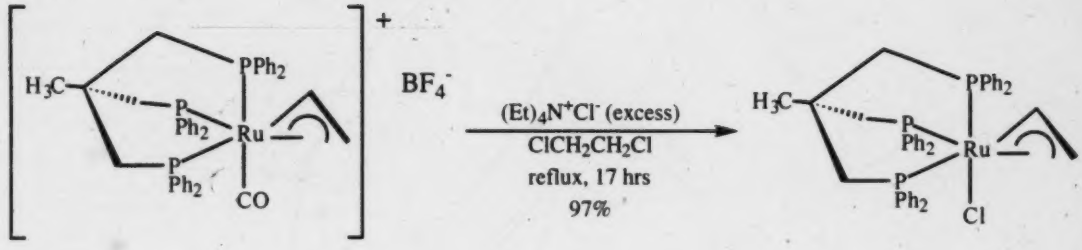
26 **27**

[(tripod)Ru(η^3-allyl)(CO)]$^+$Cl$^-$ (27). In a 5 mL round bottom flask, [(tripod)Ru(η^3-allyl)(CO)]$^+$BF$_4^-$ (55.6 mg, 63.1 mmol) and excess sodium chloride (596.3 mg, 10.20 mmol, 162 equiv) were added together with 3 mL acetone and stirred. After 30 minutes, the solvent was removed from the light yellow solution by rotary evaporation. The compound was extracted from the residue with several portions of benzene and filtered through a pad of Celite to give a transparent yellow filtrate. The solvent was removed from the filtrate *in vacuo* to give a light yellow powder (38.6 mg, 46.5 mmol, 73.7% isolated). No further purification was required. IR (KBr, $CDCl_3$, cast, cm^{-1}): 3060 (w), 2963 (w), 1997 (s, CO), 1574 (w), 1484 (m) 1434 (s), 1261 (m), 1190 (w), 1092 (vs), 1056 (vs,br), 1000 (m), 912 (m), 800 (m), 730 (s), 697 (s), 544 (m), 518 (s); ^{1}H NMR (360 MHz, $CDCl_3$): δ 7.54 (t, 4H, J = 9.3 Hz, aromatic), 7.33-7.40 (m, 10H, aromatic), 7.14-7.21 (m, 8H, aromatic), 6.92 (td, 4H, J = 7.9 Hz, 2.2 Hz, aromatic), 6.44 (virtual t, 4H, J = 9.4 Hz, aromatic), 4.83 (ddd, 1H, $J_{observed}$ = 6.3 Hz, H_c), 2.82-2.89 (m, 2H, CH_2 of tripod), 2.70-2.78 (m, 4H, CH_2 of tripod), 2.67 (d, 2H, J = 6.9 Hz, H_{syn}), 2.43 (d, 2H, J = 8.8 Hz, H_{anti}), 1.85 (d, 3H, $^4J_{P\text{-}H}$ = 3.1 Hz, CH_3); Mass Spec (Electrospray, +ve): 795 [M-Cl]$^+$, 767 [M-Cl,CO]$^+$. The halide content of **27** was confirmed by the formation of a precipitate from the reaction of **27** with a solution of silver nitrate in acetone.



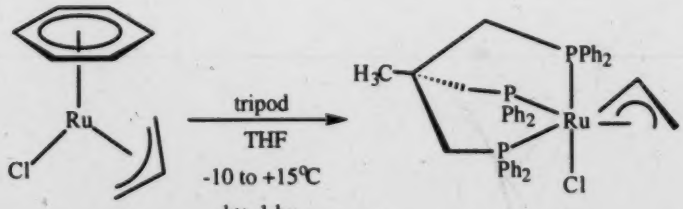
26 **28**

[(tripod)Ru(η^3-allyl)(CO)]$^+$I$^-$ (28). In a 5 mL round bottom flask, [(tripod)Ru(η^3-allyl)(CO)]$^+$BF$_4^-$ (6.1mg, 3.83 μmol) and excess sodium iodide (50.4mg, 0.384 mmol, 90.8 equiv) were added together with 1 mL acetone and stirred. The solution became bright yellow within 1 minute. After 30 minutes, the solvent was removed by rotary evaporation. The compound was extracted from this solid with several portions of benzene and filtered through a pad of Celite to give a transparent yellow filtrate. The solvent was removed from the filtrate *in vacuo* to give a yellow powder in nearly quantitative isolated yield, without further purification (3.0 mg, 3.25 μmol, 85%). IR (KBr, $CDCl_3$, cast, cm^{-1}): 3054 (w), 2962 (w), 2922 (w), 1997 (s, CO), 1484 (w), 1434 (s), 1261 (m), 1189 (w), 1092 (vs), 1034 (vs,br), 910 (m), 800 (m), 731 (s), 696 (s), 547 (m), 535 (s); ^{1}H NMR (360 MHz, $CDCl_3$) δ 7.59 (apparent t, 4H, J = 8.6 Hz, aromatic), 7.34-7.40 (m, 8H, aromatic), 7.23-7.30 (m, 2H, aromatic), 7.18 (t, 8H, J = 7.4 Hz,aromatic), 6.93 (td, 4H, J = 7.9 Hz, 2.3 Hz, aromatic), 6.49 (virtual t, 4H, J = 9.6 Hz, aromatic), 4.84 (ddd, 1H, J = 6.2 Hz, H_C), 2.93-3.00 (m, 2H, $CH_{2(axial)}$ of tripod), 2.72-2.81 (m, 4H, $CH_{2(equatorial)}$ of tripod), 2.67 (d, 2H, J = 7.0 Hz, H_{syn}), 2.48 (d, 2H, J = 9.5 Hz, H_{anti}), 2.03 (d, 3H, $^4J_{P\text{-}H}$ = 3.3 Hz, CH_3). Mass Spec (Electrospray, +ve): 795 [M-I]$^+$; Mass Spec (Electrospray, -ve): 126.9 [I]$^-$. A white precipitate formed as a result of mixing $AgNO_3$ with **28** in acetone, therefore, confirming the halide anion content of **28**.



26 **22**

[(Tripod)Ru(η^3-C_3H_5)Cl] (22) *Thermal Route*: In a 10 mL round bottom flask (on the bench top), 12.7 mg (0.0144 mmol) of [(Tripod)Ru(η^3-C_3H_5)CO]$^+BF_4^-$ (**26**) and 178.1 mg (1.075 mmol, 74.6 equiv.) of tetraethylammonium chloride were dissolved in 5 mL of 1,2-dichloroethane to form a light yellow solution. The flask was subsequently outfitted with a reflux condenser. The flask was heated in a sand bath at 100°C for 17 hours, during which time the solution turned a yellow-orange color. The solvent was removed by rotary evaporation. The product was extracted with toluene and filtered through a pad of Celite to give a transparent yellow filtrate. Solvent was removed from the filtrate *in vacuo* to give a yellow solid, 11.3 mg (0.0141 mmol, 97.8%, crude). Recrystalization from benzene gave yellow, granular crystals. However, an analytically pure sample could not be obtained despite repeated attempts of recrystallization.



29 **22**

[(Tripod)Ru(η^3-C_3H_5)Cl] (22) *Photochemical Route*: In a Schlenk tube, 74.2 mg (0.290 mmol) of [(η^6-benzene)Ru(η^3-C_3H_5)Cl] (**29**) and 188.5 mg (0.302 mmol, 1.0 equiv.) of

tripod were mixed (in air) in 5 mL of freshly distilled, anhydrous THF and then stirred rapidly for 5 minutes to give a light yellow solution. Some solid **29** remains undissolved. The flask was stoppered with a rubber septum pierced with a long syringe needle for a continuous nitrogen purge and to assist mixing. The vessel was chilled to -10°C in an ethanol bath and photoylzed for 1 hour, during which time the solution turn an orange-red color. The orange-red solution was filtered (in air) through a pad of Celite with THF to remove any residual solid. The solvent was removed from the filtrate to give an orange-red solid 220 g (0.274 mmol, 94.4% crude) of **22**. The air stable material can be recrystallized from benzene or made into a fine yellow powder by dissolving in dichloromethane and precipitating the product with hexanes (73.7%).

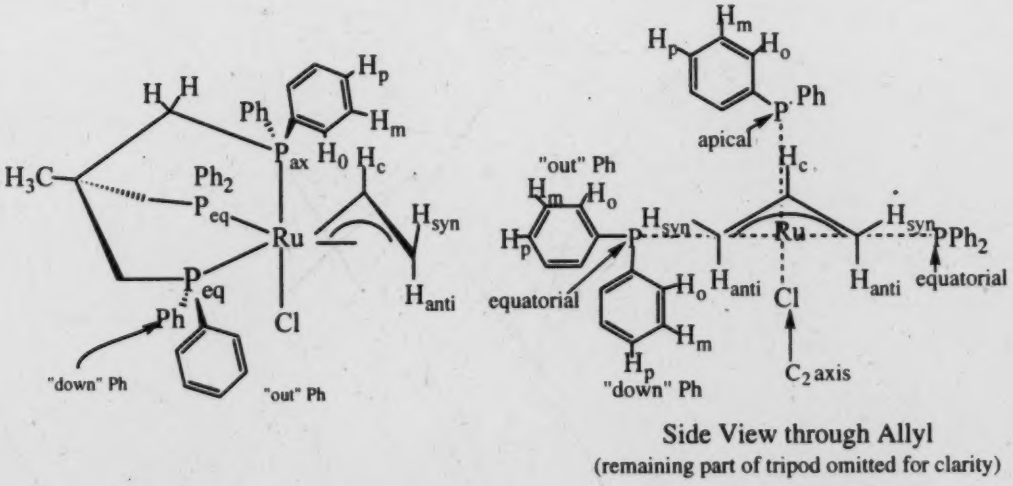
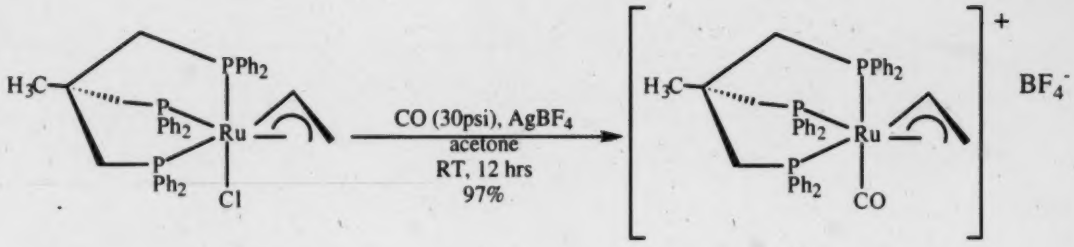


Figure 8: Labeling Scheme for Spectroscopic Assignments of Complex **22**.

IR (KBr, $CDCl_3$, cast, cm^{-1}): 3055 (w), 2953 (w), 1484 (m), 1433 (s), 1189 (w), 1092 (m), 1026 (w), 1000 (w), 910 (m), 837 (w), 729 (s), 696 (s), 642 (w), 517 (vs), 485 (m); ^1H NMR (200 MHz, CD_2Cl_2, ambient temperature) δ 7.22-7.39 (m, 12H, aromatic), 7.18 (t, 12H, $J_{observed}$ = 7.5 Hz, aromatic), 6.85 (t, 6H, $J_{observed}$= 7.5 Hz, aromatic), 6.5-7.9 (underling broad m),4.75 (m, 1H, H_c), 3.30 (d, 2H, J = 12.4 Hz, H_a), 2.86 (d, 2H, J =

7.7 Hz, H_s), 2.43 (s, 4H, $CH_{2(equatorial)}$ of tripod), 1.59 (s, 2H, $CH_{2(apical)}$ of tripod), 1.53 (d, 3H, $^4J_{P\text{-}H}$ = 2.6 Hz, CH_3 of tripod); ^1H NMR (200 MHz, CD_2Cl_2, -80 °C) δ 7.72 (broad s, 4H, aromatic), 6.90-7.55 (m, 18H, aromatic), 6.72 (t, 4H, $J_{observed}$ = 6.6 Hz, aromatic), 6.33 (t, 4H, $J_{observed}$ = 8.9 Hz, aromatic), 4.75 (m, 1H, H_c), 3.30 (slightly broad d, 2H, J = 12.4 Hz, H_a), 2.86 (slightly broad d, 2H, J = 7.7 Hz, H_s), 2.43 (s, 4H, CH_2 of tripod), 2.03 (slightly broad d, 2H, $^2J_{H\text{-}P(apical)}$ = 7.8 Hz $CH_{2(apical)}$ of tripod), 1.53 (broad s, 3H, CH_3 of tripod); $^1H\{^{31}P_{(apical)}$ irradiate at 48ppm} NMR (200 MHz, CD_2Cl_2, -80 °C) δ 7.72 (broad s, 4H, aromatic), 6.90-7.55 (m, 18H, aromatic), 6.72 (t, 4H, $J_{Hm\text{-}Ho}$ = 7.2 Hz, H_m apical phenyl), 6.33 (d, 4H, $J_{Hm\text{-}Ho}$ = 7.2 Hz, H_o apical phenyl), 4.75 (m, 1H, H_c), 3.30 (slightly broad d, 2H, J = 12.4 Hz, H_a), 2.86 (slightly broad d, 2H, J = 7.7 Hz, H_s), 2.43 (s, 4H, CH_2 of tripod), 2.03 (s, 2H, $CH_{2(apical)}$ of tripod), 1.53 (broad s, 3H, CH_3 of tripod); $^1H\{^{31}P_{(equatorial)}$ irradiate at 18ppm} NMR (200 MHz, CD_2Cl_2, -80 °C) δ 7.72 (broad m, 4H, aromatic), 6.90-7.55 (partially resolved m, 18H, aromatic), 6.72 (t, 4H, $J_{observed}$ = 6.6 Hz, aromatic), 6.33 (t, 4H, $J_{observed}$ = 8.9 Hz, aromatic), 4.75 (m, 1H, H_c), 3.30 (d, 2H, J = 12.4 Hz, H_a), 2.86 (d, 2H, J = 7.7 Hz, H_s), 2.43 (sharp s, 4H, CH_2 of tripod), 2.03 (slightly broad d, 2H, $^2J_{H\text{-}P(apical)}$ = 7.8 Hz $CH_{2(apical)}$ of tripod), 1.53 (broad s, 3H, CH_3 of tripod); $^1H\{^{31}P\}$ NMR (200 MHz, CD_2Cl_2, -40 °C) δ 7.72 (broad s, 4H, aromatic), 6.90-7.55 (m, 18H, aromatic), 6.72 (t, 4H, $J_{Hm\text{-}Ho}$ = 7.2 Hz, H_m apical phenyl), 6.33 (d, 4H, $J_{Hm\text{-}Ho}$ = 7.2 Hz, H_o apical phenyl), 4.75 (m, 1H, H_c), 3.30 (slightly broad d, 2H, J = 12.4 Hz, H_a), 2.86 (slightly broad d, 2H, J = 7.7 Hz, H_s), 2.43 (s, 4H, CH_2 of tripod), 2.03 (s, 2H, $CH_{2(apical)}$ of tripod), 1.53 (broad s, 3H, CH_3 of tripod); also see data in **Table 3** $^1H\{^{31}P\}$ NMR at -40 °C on 400 MHz; $^{31}P\{^1H\}$ (81 MHz, CD_2Cl_2, RT) δ 47.76 (broad s, 1P, P_{apical}), 18.93 (broad s, 2P, $P_{equatorial}$); $^{31}P\{^1H\}$ (81 MHz, CD_2Cl_2, -80 °C) δ 48.49 (t, 1P, $^2J_{Papical\text{-}Pequatorial}$ = 37.0 Hz, P_{apical}), 18.62 (d, 2P, $^2J_{Pequatorial\text{-}Papical}$ = 37.0 Hz, $P_{equatorial}$); $^{13}C[^1H; ^{31}P]$(75 MHz, CD_2Cl_2, -40 °C) δ 34.49(s, $\underline{C}H_3$), 37.42 (s, $\underline{C}H_{2(equatorial)}$), 37.86 (s, $C_{quaternary}$), 67.70 (s, $C_{terminal}$), 98.79 (s, $C_{central}$), 126.90-133.40 ($\underline{C}H$, aromatic),

136.82 (s, $C_{quaternary}$, aromatic), 138.85 (s, $C_{quaternary}$, aromatic), 141.67 (s, $C_{quaternary}$, aromatic); GCOSY (300MHz, CD_2Cl_2, RT) δ 2.86 (H_{syn}) ↔ δ 4.75 (H_c), δ 3.30 (H_{anti}) ↔ δ 4.75 (H_c), δ 6.85 (H_{meta}) ↔ δ 7.18 (H_{para}), δ 6.85 (H_{meta}) ↔ δ 7.22-7.39 (H_{ortho}) ; Mass Spec (Low Res.): 761 $[M-(C_3H_5)]^+$; HRMS (EI, 20 eV): 761.09253 $[M-(C_3H_5)]^+$. An analytically pure sample could not be obtained despite repeated attempts at recrystallization.



22 **26**

Generation of 26 from 22: In a Fisher-Porter bottle, 13.8 mg (0.0172 mmol) of (Tripod)Ru(η^3-C_3H_5)Cl (**22**) and 6.6 mg (0.034 mmol, 2 equiv.) of silver tetrafluoroborate were mixed. Under an atmosphere of CO, 3 mL of reagent grade acetone was added via syringe. A CO pressure of 30 psi was maintained. Within 5 minutes the solution became turbid white then quickly turned turbid brown. The mixture was stirred overnight at room temperature. The product was filtered through a pad of Celite to give a pale yellow filtrate. Solvent was removed from the filtrate in vacuo to give a white-brown solid, 14.8 mg (0.0169 mmol, 97.6%). This product was identical to that of **26** by ^{1}H NMR.

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